

Grimm, and Albrecht,⁸ that 30% of the hydrogenation is diverted to adsorbed 1,3-butadiene, 1,2-butadiene, and 1-butyne.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Kinetics of Dehydrogenation of Isobutane by Iodine and the Heat of Formation of the *t*-Butyl Radical^{1a}

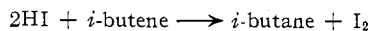
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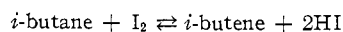
The kinetics of the gas phase thermal dehydrogenation of isobutane by I₂ to yield isobutene and HI was investigated in the temperature range from 250 to 310°. The reaction was found to proceed through an I atom and radical chain mechanism and the rate constants of the elementary steps were measured. The dissociation energy of the tertiary C-H bond in isobutane was found to be 90.9 kcal./mole at 25° and the heat of formation of *t*-butyl radical at 25° and 1 atm. was found to be 6.7 kcal./mole.

Introduction

A recent publication from this Laboratory has described the addition reaction of HI with isobutene.² The reaction above 200° proceeds homogeneously and quantitatively to yield isobutane and I₂ in accordance with the equation



and the rate-determining step, the addition of HI to isobutene, produces *t*-BuI. The equilibrium constant of the reaction



has also been studied in this Laboratory.³ It was of interest, therefore, to study the kinetics of dehydrogenation of isobutane by I₂ which might be expected to have *t*-BuI as an intermediate and for which the rate-determining step is $\text{I} + i\text{-C}_4\text{H}_{10} \rightarrow \text{t-Bu}\cdot + \text{HI}$.

From a kinetic study of the gas phase halogenation of a hydrocarbon and the accompanying inhibition of the reaction by HX, it is possible to determine the relevant C-H bond dissociation energy and also the enthalpy of formation of the corresponding radicals.⁴ However, there has been no other quantitative study on

the halogenation of isobutane except that of Eckstein, Scheraga, and Van Artsdalen.⁵ Their results on the photochemical and thermal bromination of isobutane have led to anomalous rate constants which raise doubts about the validity of the data.⁴

In the present study an effort was made to determine the reaction rate of the dehydrogenation of isobutane, to estimate the dissociation energy of the tertiary C-H bond which would be expected to dissociate at a much faster rate than the primary C-H bond and to calculate the heat of formation of the *t*-butyl radical.

Experimental

The materials and experimental apparatus used were the same as those described in the previous papers.^{3,6}

After evacuating the quartz glass cylindrical reaction vessel of 364-cc. capacity placed in an electric furnace, iodine vapor was admitted to the desired pressure by checking the absorption of light at 5000, 4900, 4800, 4600, or 4400 Å. by means of a spectrophotometer connected to an automatic recorder. Then isobutane was added and the total pressure was measured by a Bourdon spoon gage and a mercury manometer. Defining the instance of isobutane introduction as the 0-time of reaction, the absorption of I₂ thereafter was recorded continuously or at intervals, depending on the temperature at which the reaction was to be studied. The absorption of HI at 2700, 2600, and 2500 Å. was also recorded frequently throughout the reaction period.

After removing I₂ and HI, analysis of the reaction mixture by gas chromatography revealed the presence of isobutene as the

(1) (a) This work has been supported by Grants from the National Science Foundation and the U. S. Atomic Energy Commission; (b) on leave from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan.

(2) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **38**, 878 (1963).

(3) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2890 (1963).

(4) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **28**, 301 (1958).

(5) B. H. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *ibid.*, **22**, 28 (1954).

(6) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).

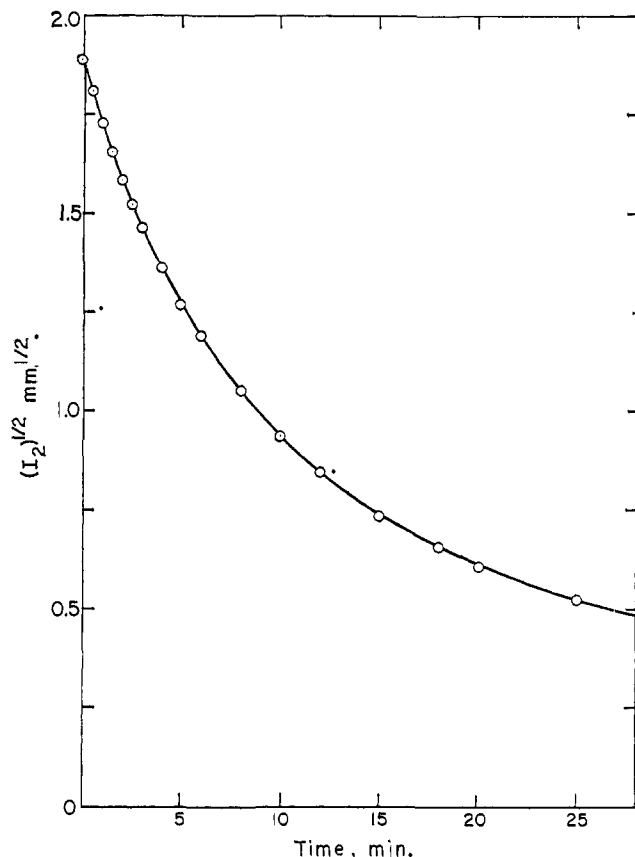


Fig. 1.— $(I_2)^{1/2}$ vs. time plot of the reaction isobutane + $I_2 \rightleftharpoons$ isobutene + $2HI$ at $582.9^\circ K$.

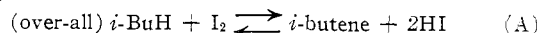
only reaction product, and the material balance between reactants and products was always within 4% with respect to both hydrocarbon and iodine.

The concentrations of isobutane ($i\text{-BuH}$) and isobutene ($i\text{-butene}$) at any reaction time were calculated from the observed (I_2) and (HI) using the stoichiometric relation

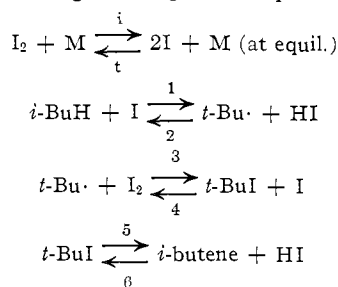
$$(i\text{-BuH}) = (i\text{-BuH})_0 - \{(I_2)_0 - (I_2)\} \text{ and} \\ (i\text{-butene}) = (I_2)_0 - (I_2) = (HI)/2$$

Mechanism

From previous work the reaction could be expected to proceed by an I atom and free radical chain mechanism. Applying the general mechanism of halogen substitution reaction with a hydrogen-donor molecule proposed and discussed by Benson and Buss,⁴ the present reaction



can be supposed to go through the steps



The termination processes such as $I + t\text{-Bu}\cdot \rightarrow t\text{-BuI}$ and $2 t\text{-Bu}\cdot \rightarrow C_8H_{18}$ would be neglected compared with the process t .

Making the stationary state assumption for $t\text{-Bu}\cdot$ and $t\text{-BuI}$, we find

$$-\frac{d(I_2)}{dt} = \frac{k_1 K_{I_2}^{1/2} (I_2)^{1/2} (i\text{-BuH}) [1 - B]}{1 + \frac{k_2 (HI)}{k_3 (I_2)} \left[1 + \frac{k_1 (I)}{k_5} \right]} \quad (1)$$

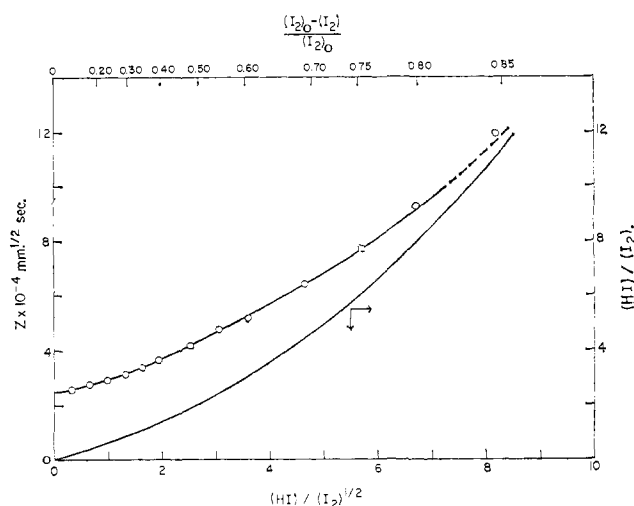


Fig. 2.— Z vs. $(HI)/(I_2)^{1/2}$ plot and $(HI)/(I_2)$ vs. $(HI)/(I_2)^{1/2}$ relation of a run at $582.9^\circ K$. Circles are experimental points and curve is calculated (eq. 4).

where K_{I_2} is the equilibrium constant for I atom formation; $B \equiv (i\text{-butene})(HI)^2 / K(i\text{-BuH})(I_2)$, the correction term for the back reaction; and K is the equilibrium constant of the over-all reaction (A).

Denoting $S \equiv -d(I_2)^{1/2}/dt$, we have

$$\frac{(i\text{-BuH})[1 - B]}{2S} = \frac{1}{k_1 K_{I_2}^{1/2}} + \frac{k_2 k_4 (HI)(I)}{k_3 k_5 k_1 K_{I_2}^{1/2} (I_2)} + \frac{k_2 (HI)}{k_3 k_1 K_{I_2}^{1/2} (I_2)} \quad (2)$$

Substituting the relations $k_1 k_3 k_5 / k_2 k_4 = k_6 K$ and $(I) = K_{I_2}^{1/2} (I_2)^{1/2}$ into the second term of the right-hand side of eq. 2, the rate equation becomes

$$\frac{(i\text{-BuH})[1 - B]}{2S} = \frac{1}{k_1 K_{I_2}^{1/2}} + \frac{1}{k_6 K} \times \frac{(HI)}{(I_2)^{1/2}} + \frac{k_2}{k_3 k_1 K_{I_2}^{1/2}} \times \frac{(HI)}{(I_2)} \quad (3)$$

or

$$\frac{(i\text{-BuH})[1 - B]}{2S} \equiv Z = a_1 + a_2 \frac{(HI)}{(I_2)^{1/2}} + b \frac{(HI)}{(I_2)} \quad (4)$$

where a_1 , a_2 , and b are constants at a given temperature and

$$a_1 = 1/k_1 K_{I_2}^{1/2}, \quad a_2 = 1/k_6 K, \quad \text{and} \quad b = k_2/k_3 k_1 K_{I_2}^{1/2} = a_1(k_2/k_3).$$

Since k_6 , the rate constant of reaction step 6,² and K , the equilibrium constant of the over-all reaction,³ have been measured in the previous work, we can calculate the value of a_2 . The values of a_1 and b can be determined from any two points on the smoothed curve of the experimental results plotted on a Z vs. $(HI)/(I_2)^{1/2}$ graph. Hence, using the $K_{I_2}^{1/2}$ values calculated from the thermodynamic data, we can determine k_1 and k_2/k_3 , the "inhibition" constant.

Results

The kinetic measurements were carried out in the range $525.1 \sim 582.9^\circ K$. The experimental conditions and the results obtained are listed in Table I. The typical example of the $(I_2)^{1/2}$ vs. time plot is shown in Fig. 1 and the respective Z vs. $(HI)/(I_2)^{1/2}$ plot in Fig. 2. No induction period is observable, in agreement with the estimate by Benson and Buss⁴ that at $560^\circ K$. the time for attainment of 90% of the stationary state concentration of I atom from I_2 should be less than 0.1 sec. The smoothed curve of the experimental data plotted in Fig. 2 is well fitted by eq. 4 where the coefficients a_1 , a_2 , and b are 2.46×10^4 mm.^{1/2} sec., 0.240×10^4 sec., and 0.625×10^4 mm.^{1/2} sec., respectively. The value of a_2 is calculated from the

TABLE I
 RATE CONSTANT DATA FOR THE *i*-BUTANE + I₂ REACTIONS

Temp., °K.	Initial pressure, mm.		$a_2 \times 10^{-4}$, sec.	$a_1 \times 10^{-4}$, mm. ^{1/2} sec.	$b \times 10^{-4}$, mm. ^{1/2} sec.	k_1 , l./mole-sec.	k_2/k_3	$k_4 \times 10^{-5b}$
	(<i>i</i> -BuH) ₀	(I ₂) ₀						
525.1	200.3	9.67	13.9	94.7	21.8	91.5	0.230	1.9
525.7	275.4	3.89	13.2	90.0	20.0	94.4	0.222	2.0
							Av. 0.226	
551.9	206.5	7.50	1.75	14.3	3.28	272	0.230	4.1
552.5	121.2	14.8	1.68	14.8	3.26	259	.223	4.0
552.5	158.7	4.32	1.68	15.0	3.77	256	.251	3.5
							Av. 0.234	
582.7	131.9	8.37	0.242	2.47	0.607	693	0.245	6.9
582.7	168.8	5.95	.242	2.70	.685	634	.254	6.1
582.9	136.7	3.56	.240	2.46	.625	692	.254	6.7
							Av. 0.251	

^a Calculated from the values of k_6 and K (see ref. 2 and 3) ^b Calculated by using K_{eq} estimated from the thermodynamic data in Table II.

values of k_6 and K reported previously. From the value of a_1 , that is the intercept of the curve at the axis of $(HI)/(I_2)^{1/2} = 0$, k_1 is calculated using K_{I_2} value estimated from the thermodynamic data shown in Table II. The inhibition constant, k_2/k_3 , can also be determined from a_1 and b . The results of these calculations are listed in Table I.

 TABLE II
 THERMODYNAMIC DATA^a

Compounds	ΔH_f , kcal./mole	S° , cal./mole- °K.	C_p° , cal./mole- °K.
I ₂	14.9	62.3	8.8
I	25.5	43.2	5.0
H	52.1	27.4	5.0
HI	6.2	49.3	7.0
<i>i</i> -BuH	-32.1	70.4	23.1
<i>i</i> -Butene	-4.0	70.2	21.3
<i>t</i> -BuI ^b	-17.2	82.5	28.3

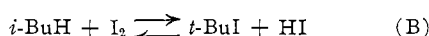
^a Unless otherwise noted all values are from NBS Circular No. 500 or API Compilation. Standard States are ideal gases at 1 atm., 25°. ^b S. W. Benson and A. Amano, *J. Chem. Phys.*, **37**, 197 (1962).

From the Arrhenius plot of the rate constant k_1 shown in Fig. 3, we find the equation

$$\log k_1 = 10.88 - \frac{21400}{4.575T} \quad (5)$$

The estimated precision of the activation energy is $E_1 = 21.4 \pm 0.5$ kcal./mole with corresponding precision in the A -factor, $\log A_1 = 10.88 \pm 0.15$. Eckstein, Scheraga, and Van Artsdalen reported the A -factor for the reaction $t\text{-BuH} + \text{Br} \rightarrow t\text{-Bu}\cdot + \text{HBr}$ as 3.76×10^{14} (l./mole) sec.⁻¹ at 403.4°K., which was abnormally higher than the collision number and the steric factor reported as 2740. In the present case, using 4.2 Å. as the collision diameter of iodine atom and 4.6 Å. for that of isobutane molecule, the collision number at 553°K. is found to be 1.95×10^{11} (l./mole unit) sec.⁻¹ and hence the steric factor is 0.39 which seems to be a quite reasonable one.

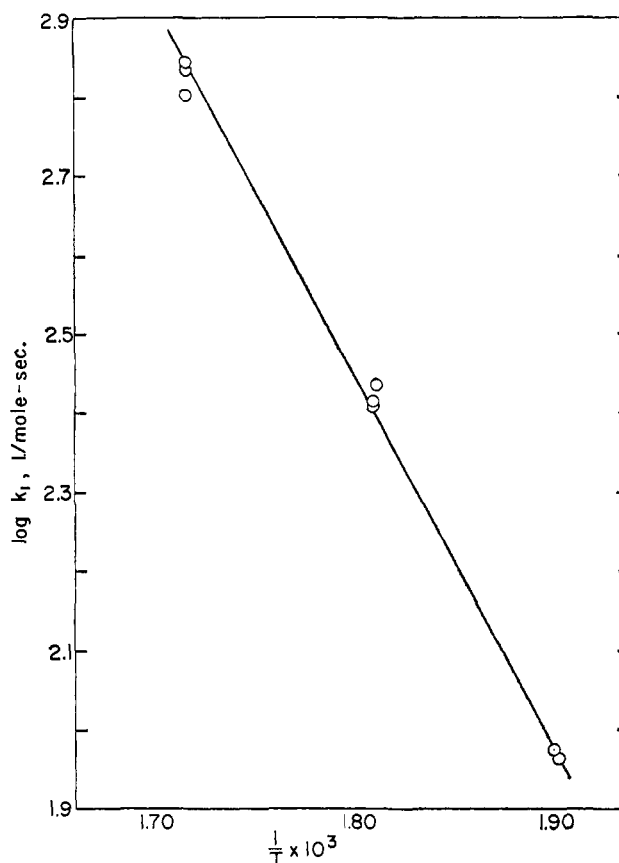
The rate constant for the step 4, k_4 , can also be calculated by using the relation $k_1 k_3 / k_2 k_4 = K_{eq}$, where K_{eq} is the equilibrium constant of the reaction



K_{eq} is computed from the thermodynamic data in Table II. The values of k_4 thus obtained are shown in the last column of Table I, and from the Arrhenius plot k_4 is best fitted as

$$\log k_4 = 10.7 - \frac{13000}{4.575T} \quad (6)$$

Considering the errors of these calculations, the activation energy E_4 will be 13.0 ± 0.7 kcal./mole and $\log A_4 = 10.7 \pm 0.4$ in the temperature range of the pres-


 Fig. 3.—Arrhenius plot of k_1 .

ent experiment. The value of A_4 is very close to 8×10^{10} l./mole-sec. for all the alkyl iodides.⁷

The values of E_1 and E_4 give the value of $E_2 - E_3$ as

$$E_2 - E_3 = E_1 - E_4 - \Delta H_B = 21.4 - 13.0 - 7.0 = 1.4 \text{ kcal./mole} \quad (7)$$

where ΔH_B is the heat of reaction of eq. B at the experimental temperature range and is calculated to be 7.0 ± 0.5 kcal./mole from the data in Table II. The values 1.4 ± 0.7 kcal. for $E_2 - E_3$ is in accordance with expectation for these types of reactions.⁸ Using the

(7) S. W. Benson, *J. Chem. Phys.*, **38**, 1945 (1963).

(8) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

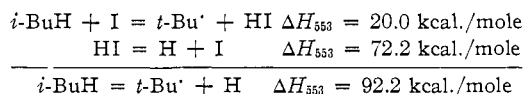
ΔS_B the entropy change of eq. B calculated from the thermodynamic data, $\log (A_2/A_3)$ is also given as

$$\log (A_2/A_3) = 10.88 - 10.7 - 0.26 = -0.08 \approx 0 \quad (8)$$

and $A_2/A_3 \approx 1$ is quite reasonable.

As shown in Table I, the values of inhibition constant k_2/k_3 changes from 0.226 to 0.251 depending on the temperature change of about 60°K., that is about 11% increase, and the average k_2/k_3 value is 0.24. The latter value gives, assuming $A_2/A_3 = 1$, 1.6 kcal./mole for $E_2 - E_3$, and this result shows good coincidence with the results of eq. 7. From $E_2 - E_3 = 1.6$ we find $(k_2/k_3)_{583^\circ} / (k_2/k_3)_{523^\circ} \approx 1.16$, that is, 16% increase with the temperature change of 60°K., and this result also shows good coincidence with those of experimental results.

Assuming $E_3 \approx 0$, E_2 may be considered as 1.4 kcal./mole at 523 ~ 583°K. Thus the heat of formation of the step 1 is given as 20.0 ± 0.7 kcal./mole. The bond dissociation energy of tertiary C-H bond, that is, the enthalpy change for the reaction $i\text{-BuH} \rightarrow t\text{-Bu}\cdot + \text{H}$, can be given as follows.



If we assume that the heat capacities of isobutane and the t -butyl radical are approximately equal, then the bond dissociation energy at 25°, $D^\circ(t\text{-Bu-H})$, is calculated as 90.9 ± 0.7 kcal./mole, which shows good coincidence with 91.1 ± 0.5 kcal./mole given by Eckstein, Scheraga, and Van Artsdalen from their bromination experiments.⁹

From the value of 90.9 kcal./mole for the bond dissociation energy, the heat of formation of the t -butyl radical is given as

$$\begin{aligned} \Delta H_f^\circ(t\text{-Bu}\cdot) &= \Delta H_f^\circ(i\text{-BuH}) - \Delta H_f^\circ(\text{H}) + D^\circ(t\text{-Bu-H}) \\ &= -32.1 - 52.1 + 90.9 = 6.7 \text{ kcal./mole} \end{aligned}$$

Hence the heat of formation of the t -butyl radical at 25° and 1 atm. is 6.7 ± 0.7 kcal./mole.

(9) This agreement unfortunately can only be looked upon as an extraordinary coincidence since the corresponding value of $E_2 - E_3 = 8$ kcal. found for the bromine system is quite unreasonable and unbelievable. It requires $A_2/A_3 \approx 10^6$ which is equally unbelievable.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Thermodynamics of the Homogeneous, Gas Phase Dehydrogenation of Isobutane^{1a}

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The gas-phase equilibrium of the reaction $i\text{-C}_4\text{H}_{10} + \text{I}_2 \rightleftharpoons i\text{-C}_4\text{H}_8 + 2\text{HI}$ has been studied in the temperature range 522.5 to 582.9°K., analyzing for I_2 and HI *in situ*, spectrophotometrically. The experimental data yield for the equilibrium constant, $\log K_p(\text{atm.}) = -(25900 \pm 300)/4.575T + 8.130$. The mean deviation of the experimental points from this line is 1%. From the thermodynamic properties of the pure substances found in the literature it is possible to calculate ΔH and ΔS values of 26.1 kcal. and 37.3 Gibbs/mole, which compare very well with 25.9 kcal. and 37.2 Gibbs/mole from the above equation. If we further subtract off the contribution of 2HI and I_2 which are known spectroscopically with great precision, we obtain values of ΔH_d and ΔS_d for the dehydrogenations, which agree with calculated values to 0.2 kcal. and 0.2 Gibbs/mole, respectively, over the entire temperature range. It appears that I_2 can be used in this fashion to obtain precise data on many equilibria which are otherwise difficult to observe.

Introduction

Recent investigations in these laboratories of the addition reactions of I_2 ² or HI ^{3a,b} to simple olefins have led to an elucidation of the thermodynamics and kinetics of the reactions of alkyl radicals with HI and I_2 . It was of interest, therefore, to examine the reverse reaction, that is, the homogeneous, gas-phase, dehydrogenation of paraffin hydrocarbon by I_2 which goes to produce the corresponding olefin and HI .

Isobutane was selected as the paraffin, from the viewpoints that: (1) the reaction isobutene + 2HI → isobutane + I_2 was recently studied in these laboratories and found to proceed homogeneously and quantitatively above 200°,³ and (2) isobutane contains a tertiary C-H bond which would be expected to be more reactive than the primary one and so the dehydrogenation reaction would go at an appropriate rate in a convenient temperature range.

As to the gas-phase reaction isobutane + $\text{I}_2 \rightleftharpoons$ isobutene + 2HI, there has been no study of its thermochemistry. In the present study the equilibrium constant of the reaction is measured to ±3% over a broad composition and temperature range. This, together with thermal data on I_2 and HI , yield data on the free

energy of hydrogenation of isobutene at high temperatures which are accurate to about ±0.05 kcal.

Experimental

The experimental apparatus was the same as that described in a previous paper.⁴

The concentrations of I_2 and HI were estimated from their optical densities measured by means of a spectrophotometer. The sample beam of a Beckman Model DB spectrophotometer went longitudinally through a quartz glass cylindrical reaction vessel of 364-cc. capacity and 20.0-cm. length placed in an aluminum block furnace. Temperature of the furnace was maintained to within ±0.2° by an Electrotherm controller in conjunction with a Wheatstone bridge having platinum resistance as one arm of it and the reaction temperature was measured by a copper-constantan thermocouple placed in the reaction vessel.

A tungsten bulb served as a visible light source while a hydrogen lamp was used for an ultraviolet light source. An ethanol-water mixture containing a slight amount of CCl_4 was used as the reference liquid in order to make flat the background of the absorption spectrogram in the region of wave length from 5000 to 2400 Å. The relation between optical densities and concentration was measured at 5000, 4900, 4800, 4600, 4400, 4200, 3000, 2700, 2600, 2500, and 2400 Å. for I_2 , and 3000, 2700, 2600, 2500, and 2400 Å. for HI , respectively, by using silicone oil manometer and Bourdon spoon gage. Up to about 5 mm., I_2 concentration was estimated from the absorption at 4900, 4800, and 5000 Å., and for higher pressure 4600 and 4400 Å. were used. For HI , 2700 and 2600 Å. were used mainly after correcting for the small absorption of I_2 at these wave lengths. From these calibration curves the concentrations of I_2 and HI were estimated with an accuracy of ±2%. At low concentrations below 1 mm. the background noise contributed an error of about ±0.02 mm.

(1) (a) This work has been supported by grants from the National Science Foundation and the U. S. Atomic Energy Commission; (b) on leave from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan.

(2) S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962).

(3) (a) A. N. Bose and S. W. Benson, *ibid.*, **37**, 1081 (1962); (b) **38**, 878 (1963).

(4) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).