742 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 742—748 (1981) [Vol. 54, No. 3

Kinetics of the Catalytic Decomposition of Hydrogen Iodide in the Magnesium-Iodine Thermochemical Cycle

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(Received July 11, 1980)

The decomposition of hydrogen iodide serves as the hydrogen-evolution step in several thermochemical water-splitting cycles, including the Magnesium–Iodine cycle. A kinetic analysis of the catalytic decomposition of hydrogen iodide has been carried out by the use of a flow method at 500—700 K. The platinum-supported active carbon catalyst (1 wt%) and the active carbon catalyst which have been found effective in the research reported previously, are used as the catalysts. The contact time-conversion relationships for both the catalysts are simulated successfully on the basis of an assumed reaction scheme. The influence of water vapor on the rate and the equilibrium of the decomposition of hydrogen iodide is negligibly small. The inhibition effect of iodine on the rate of the decomposition of hydrogen iodide over the platinum-supported active carbon catalyst is remarkable below 550 K.

The decomposition of hydrogen iodide serves as the hydrogen-evolution step in several thermochemical water-splitting cycles,[1–4] including the Magnesium–Iodine cycle[5] previously proposed by the present authors. It is favorable for the reaction to be carried out around or below 700 K from the standpoint of the construction of the present cycle. However, since the rate of the reaction in the form of a homogeneous gas-phase reaction is low in the temperature range below 700 K, the present authors attempted to carry out the reaction catalytically.

In the first step of the study of the catalytic decomposition of hydrogen iodide, a screening test of various catalysts prepared by an impregnation method from the compounds of all the members of the first transition-metal series, from the compounds of the members of the platinum-group metals, and so on, and from various catalyst supports were carried out. In the research, a platinum-supported active carbon catalyst (abbreviated as the Pt/C catalyst) and an active carbon catalyst were found to reveal favorable catalytic activities.[6]

For the second step of the research, a kinetic analysis of the reaction, a quantitative investigation of the influence of iodine and water vapor that may coexist with the hydrogen iodide to be decomposed on the rate and the equilibrium of the reaction, and a life test of the catalysts were necessary.

There have been very few reports on the kinetic studies of the decomposition of hydrogen iodide. Hinshelwood and Burk,[7] however, reported that the reaction over platinum wire under the conditions of a continuous removal of the iodine formed proceeded according to the following rate equation:

$$-\frac{dP_{HI}}{dt} = k,$$

where P_{HI} is the partial pressure of hydrogen iodide and where k is the rate constant. Iida[8] reported recently that the reaction over platinum supported on Teflon under the conditions of a continous removal of the iodine formed proceeded according to the following rate equation:

$$-\frac{dP_{HI}}{dt} = \frac{P_{HI}}{14.76P_{H_2}+7.49P_{HI}+208},$$

where P_{HI} is the partial pressure of hydrogen iodide, and so on. In both the researches, the reaction systems were simplified by the continuous removal of the iodine formed. The results of both the researches gave only insufficient information, however, on the unresolved questions related to thermochemical water splitting.

Therefore, the present authors have investigated the influence of the contact time and the partial pressure of hydrogen iodide, iodine, and water vapor on the reaction rate over the Pt/C catalyst and the active carbon catalyst, and analyzed the results on the basis of an assumed reaction scheme. They have also examined the lifetime of both the catalysts and the water-gas reaction of the carbon used as a catalyst or a support. On the basis of the results, it was confirmed that both the catalysts can be used for the decomposition of hydrogen iodide in the presence of water vapor at 550—700 K.

Experimental

The Pt/C catalyst (1.05 wt%) was prepared from the active carbon (Shirasagi-C granular, Takeda) and $H_2PtCl_6 \cdot 6H_2O$ by an impregnation-calcination method (Ar stream, 1000 K, 6 h), and was ground to a diameter of less than 0.30 mm (0.30—0.15 mm, 47 wt%; 0.15—0.03 mm, 42 wt% <0.03 mm, 11 wt%) before use. The active carbon catalyst was prepared by a calcination-grinding treatment of the active carbon similar to that used for the Pt/C catalyst. The experiments were carried out by the use of a tubular reactor with the aid of argon carrier gas. The apparatus was similar to that depicted in the preceding paper.[6] Hydrogen iodide was fed in the form of hydriodic acid (7.5 mol l^{-1}, Wako, Sp. Gr.) to obtain reaction conditions similar to those in the decomposition of hydrogen iodide included in the present thermochemical cycle, in which a certain amount of water vapor might coexist with hydrogen iodide. The reactant and the carrier gas were fed in at the following rates: HIaq, 32.3 ml/h; Ar, 9.0 l/h ($P_{HI}=0.125$ atm, $P_{H_2O}=0.682$, $P_{Ar}=0.193$), unless otherwise stated. In all cases, the reactions were carried out under a total pressure equal to 1 atm. The contact time was varied by varying the catalyst amount at a fixed feed rate of the reactants and the carrier gas. The catalyst amount of 1.71 g (for both the Pt/C catalyst and the active carbon catalyst) corresponded to the contact time of 2.86×10^{-1} s (S.V.$=1.26 \times 10^4$ h^{-1}). All the exhaust components except for hydrogen and argon were condensed out in the scrubber. The hydrogen concentration of the exhaust gas was determined by the use of gas chromatography (YANACO, G180) with a molecular sieve 13 X column, while the flow rate of the exhaust gas (H_2+Ar) was measured with a soap-film flowmeter. The conversions of hydrogen iodide at each temperature were monitored by measuring the hydrogen concentration of the exhaust gas for about 1 h. After the concentration had become constant, the conversions were determined in each run in the directions of both the decreasing and increasing temperatures by taking the flow rate of the exhaust gas into account. The steady state of the reaction was confirmed by the close agreement of both conversions at each temperature. As the conversion in the blank experimentation was low (5.3×10^{-5} (600 K), 4.5×10^{-4} (650 K), 1.6×10^{-3} (700 K), it was clear that both the thermal decomposition in the gas phase and the catalytic decomposition on the surface of the glass wall of apparatus were negligible. The relative error in the conversion measurement was, in general, less than 4%.

Results and Discussion

Water-gas Reaction and Life Test. Active carbon is consumed through the reaction with water vapor, yielding hydrogen and carbon monoxide at high temperatures.

$$C + H_2O \longrightarrow H_2 + CO;\ \text{water-gas reaction}$$

It was assumed that the life of both catalysts for the decomposition of hydrogen iodide in the presence of water vapor was mainly dependent on the rate of the water-gas reaction. The rate of the hydrogen evolution through the reaction of both the catalysts with water vapor was measured. The results are presented in Table 1. The rate over the Pt/C catalyst was higher than that over the active carbon catalyst over the whole range of temperatures studied. It would be desirable to use the former catalyst below 700 K or the latter below 800 K to avoid a catalyst loss through the water-gas reaction. The conversion of hydrogen iodide over the Pt/C catalyst (0.171 g, 650 K) or the active carbon catalyst (0.570 g, 700 K) was confirmed to remain almost unchanged after 100 h of operation under the following feed rates: HIaq, 36.2 ml/h; Ar, 4.5 l/h.

Table 1. Hydrogen evolution rate through water-gas reaction

T/K	Pt/C ml(STP)/h	Active carbon ml(STP)/h
500	0	0
600	0.2	0
700	2.2	0.1
800	9.5	0.4

Effect of Mass Transfer on the Reaction Rate.[9–11] When 0.171 g of the Pt/C catalyst was used, the ratio of the length of the catalyst layer to the average diameter of the catalyst particle was about 15. As it is accepted that the back-mixing effect is negligible when the ratio is about 20 or more, the back-mixing effect was almost negligible in the present experiment.

Both the feed rate and the catalyst amount were varied at a fixed contact time (2.86×10^{-2} s) over the Pt/C catalyst that shows a higher catalytic activity of the two kinds of catalysts: HIaq 32.3 ml/h, Ar 9.0 l/h, Pt/C 0.171 g and HIaq 21.5 ml/h, Ar 6.0 l/h, Pt/C 0.114 g. As the conversions were almost the same for each feed rate at 500—700 K, the external film diffusion did not seem to influence the reaction rate in this range of feed rates.

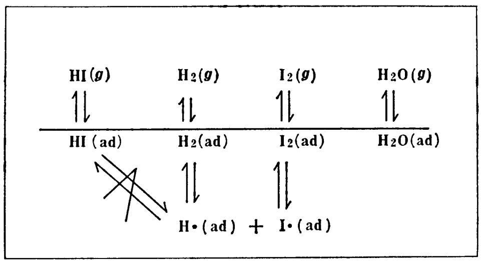


Fig. 1. Assumed reaction scheme for the catalytic decomposition of hydrogen iodide over the Pt/C catalyst or the active carbon catalyst in the presence of water vapor.

The conversion by the use of the Pt/C catalyst with a particle diameter of less than 0.15 mm differed little from that over the Pt/C catalyst with a diameter of less than 0.30 mm at a contact time of 1.43×10^{-2} s at 500—700 K. Therefore, the effect of internal diffusion in the micro pore of the catalyst on the reaction rate was considered to be insignificant.

Reaction Scheme. As the basis of the kinetic analysis of the catalytic decomposition of hydrogen iodide over the Pt/C catalyst or the active carbon catalyst, an appropriate reaction scheme was assumed. In the preceding paragraph, the effect of mass transfer on the reaction rate was shown to be negligibly small under the present experimental conditions. Therefore, the present authors assumed, on the basis of the results obtained by Hinshelwood and Burk[7] and Iida[8] that: (i) the reaction proceeds according to the reaction scheme depicted in Fig. 1 and (ii) the reaction kinetics can be analyzed according to a Langmuir-Hinshelwood type of mechanism.

Under the above assumption, the rate equation of the decomposition of hydrogen iodide, V_f, is written as follows, where k_f is the rate constant of the first-order surface reaction and θ_{HI} is the surface coverage by hydrogen iodide:

$$V_f = -\frac{dP_{HI}}{dt} = k_f\theta_{HI}. \quad (1)$$

θ_{HI} is written as follows, where K_{HI} is the adsorption coefficient of hydrogen iodide, p_{HI} is the partial pressure of hydrogen iodide, K_H is the adsorption coefficient of dissociated hydrogen, and so on:

$$\theta_{HI} = \frac{K_{HI}P_{HI}}{1+K_{HI}P_{HI}+K_{H_2}P_{H_2}+\sqrt{K_HP_{H_2}}+K_{I_2}P_{I_2}+\sqrt{K_IP_{I_2}}+K_{H_2O}P_{H_2O}}. \quad (2)$$

As has been mentioned above, Iida found that the rate equation of the catalytic decomposition of hydrogen iodide over the Pt/Teflon was expressed as follows under his experimental conditions:

$$-\frac{\mathrm{d}P_{\mathrm{HI}}}{\mathrm{d}t}=\frac{P_{\mathrm{HI}}}{14.76P_{\mathrm{H_2}}+7.49P_{\mathrm{HI}}+208}. \tag{3}$$

In Eq. 3, no term corresponding to the dissociated chemical species is included. Therefore, the present authors eliminate $\sqrt{K_{\mathrm{H}}P_{\mathrm{H_2}}}$ and $\sqrt{K_{\mathrm{H}}P_{\mathrm{I_2}}}$ from Eq. 2 as negligible and thus obtain the following equation:

$$\theta_{\mathrm{HI}}=\frac{K_{\mathrm{HI}}P_{\mathrm{HI}}}{1+K_{\mathrm{HI}}P_{\mathrm{HI}}+K_{\mathrm{H_2}}P_{\mathrm{H_2}}+K_{\mathrm{I_2}}P_{\mathrm{I_2}}+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}}. \tag{4}$$

P_{HI}, $P_{\mathrm{H_2}}$, and $P_{\mathrm{I_2}}$ are expressed as follows under the conditions that no condensed phase is present, where P is the initial partial pressure of hydrogen iodide and where x is the conversion of hydrogen iodide:

$$\left.\begin{aligned}P_{\mathrm{HI}}&=P(1-x)\\P_{\mathrm{H_2}}&=Px/2\\P_{\mathrm{I_2}}&=Px/2\end{aligned}\right\}. \tag{5}$$

Substituting Eq. 5 in Eq. 4, Eq. 6 is obtained:

$$\theta_{\mathrm{HI}}=\frac{PK_{\mathrm{HI}}(1-x)}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P+(K_{\mathrm{H_2}}/2+K_{\mathrm{I_2}}/2-K_{\mathrm{HI}})Px}. \tag{6}$$

With Eq. 1 and Eq. 5, Eq. 7 is obtained:

$$-\frac{\mathrm{d}P_{\mathrm{HI}}}{\mathrm{d}t}=-\frac{\mathrm{d}(P(1-x))}{\mathrm{d}t}=\frac{P\mathrm{d}x}{\mathrm{d}t}=k_{\mathrm{f}}\theta_{\mathrm{HI}}. \tag{7}$$

Substituting Eq. 6 in Eq. 7, the following equation is given:

$$\begin{aligned}\frac{P\mathrm{d}x}{\mathrm{d}t}&=\frac{k_{\mathrm{f}}PK_{\mathrm{HI}}(1-x)}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P+(K_{\mathrm{H_2}}/2+K_{\mathrm{I_2}}/2-K_{\mathrm{HI}})Px}\\&=\frac{\dfrac{k_{\mathrm{f}}PK_{\mathrm{HI}}(1-x)}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P}}{1+\dfrac{(K_{\mathrm{H_2}}/2+K_{\mathrm{I_2}}/2-K_{\mathrm{HI}})Px}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P}}.\end{aligned} \tag{8}$$

Consequently, the rate equation for the catalytic decomposition of hydrogen iodide is expressed by Eq. 9:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k(1-x)}{1+ax}, \tag{9}$$

where:

$$a=\frac{(K_{\mathrm{H_2}}/2+K_{\mathrm{I_2}}/2-K_{\mathrm{HI}})P}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P} \tag{10}$$

$$k=\frac{k_{\mathrm{f}}K_{\mathrm{HI}}}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P}. \tag{11}$$

As the reaction rate of the formation of hydrogen iodide from hydrogen and iodine, V_{b} is proportional to the product of the surface coverage by the dissociated hydrogen and that by the dissociated iodine, according to the reaction scheme assumed in Fig. 1, V_{b} is expressed as follows, where k_{b} is the rate constant of the formation of hydrogen iodide:

$$V_{\mathrm{b}}=\frac{\mathrm{d}P_{\mathrm{HI}}}{\mathrm{d}t}=k_{\mathrm{b}}\theta_{\mathrm{H}}\theta_{\mathrm{I}}. \tag{12}$$

θ_{H} and θ_{I} are expressed as follows by a treatment similar to that for Eq. 4;

$$\theta_{\mathrm{H}}=\frac{\sqrt{K_{\mathrm{H}}P_{\mathrm{H_2}}}}{1+K_{\mathrm{HI}}P_{\mathrm{HI}}+K_{\mathrm{H_2}}P_{\mathrm{H_2}}+K_{\mathrm{I_2}}P_{\mathrm{I_2}}+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}} \tag{13}$$

$$\theta_{\mathrm{I}}=\frac{\sqrt{K_{\mathrm{I}}P_{\mathrm{I_2}}}}{1+K_{\mathrm{HI}}P_{\mathrm{HI}}+K_{\mathrm{H_2}}P_{\mathrm{H_2}}+K_{\mathrm{I_2}}P_{\mathrm{I_2}}+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}}. \tag{14}$$

Equation 15 is obtained by substituting Eqs. 5, 13, and 14 into Eq. 12:

$$-\frac{P\mathrm{d}x}{\mathrm{d}t}=\frac{\dfrac{k_{\mathrm{b}}Px\sqrt{K_{\mathrm{H}}K_{\mathrm{I}}}}{2(1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P)^2}}{\left(1+\dfrac{(1+K_{\mathrm{H_2}}/2+K_{\mathrm{I_2}}/2-K_{\mathrm{HI}})Px}{1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P}\right)^2}. \tag{15}$$

Equations 15 is transformed to give Eqs. 16 and 17:

$$-\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k'x}{(1+ax)^2}, \tag{16}$$

where:

$$k'=\frac{k_{\mathrm{b}}\sqrt{K_{\mathrm{H}}K_{\mathrm{I}}}}{2(1+K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}+K_{\mathrm{HI}}P)^2} \tag{17}$$

and where P is the initial partial pressure of hydrogen iodide.

Consequently, combining Eq. 9 with Eq. 16 gives the rate equation of the catalytic decomposition of hydrogen iodide, including the backward reaction:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k(1-x)}{1+ax}-\frac{k'x}{(1+ax)^2}. \tag{18}$$

Integrating Eq. 18 under the initial conditions (when t equals zero, x equals zero) and the equilibrium conditions (when x equals x_{e}, the equilibrium conversions of hydrogen iodide, $\mathrm{d}x/\mathrm{d}t$ equals zero) yields the following expression:

$$\begin{aligned}-kt=ax&+\frac{(ax_{\mathrm{e}}^2+2x_{\mathrm{e}}-1)}{x_{\mathrm{e}}}\ln\left(\frac{x_{\mathrm{e}}-x}{x_{\mathrm{e}}}\right)\\&+\frac{(x_{\mathrm{e}}-1)^2}{x_{\mathrm{e}}(ax_{\mathrm{e}}^2+1)}\ln\frac{(x_{\mathrm{e}}-x)}{x_{\mathrm{e}}(ax_{\mathrm{e}}x-1)},\end{aligned} \tag{19}$$

where k and a are expressed as in Eqs. 10 and 11 respectively.

Thus, the contact time-conversion relationship of the catalytic decomposition of hydrogen iodide is expressed by the Rate Equation 19, which has two constants independent of the contact time: k, mainly concerned with the reaction rate, and a, mainly concerned with the adsorption.

Contact Time-Conversion Relationship. The experimental results obtained over the Pt/C catalyst and the active cabon catalyst are depicted as the points in Figs. 2 and 3. The error in the measurement of the conversion of hydrogen iodide caused by the water-gas reaction, significant only in the case of the Pt/C catalyst at 700 K, was corrected by assuming that the rate of hydrogen evolution by the water-gas reaction was proportional to both the feed rate of water vapor and the amount of the catalyst. The results were simulated on the basis of Eq. 19. By considering the form of the equation, the simulation of the experimental results was performed by first determining the value of a which gave the least coefficient of variation of k, $(((k_i\text{-}\bar{k})^2/n)^{1/2}/\bar{k})$, then, the value of k as the average of k corresponding to the respective data in each run by employing the value of the a. The values

Table 2. Values of k, a, and x_e(equilibrium conversion) for Eq. 20

T/K	Pt/C		Active carbon		x_e
	k/s	a	k/s	a	
500	4.45×10^{-1}	3.75×10	1.78×10^{-1}	1.92×10^{2}	0.151
550	1.47	1.47×10	7.46×10^{-1}	9.66×10	0.166
600	3.64	2.76	1.06	2.21×10	0.182
650	8.47[a)]	1.20[a)]	1.44	2.90	0.195
700	1.71×10[a)]	5.10×10^{-1}[a)]	2.25	5.74×10^{-1}	0.210

a) As the number of the effective data for the calculation is small, both k and a are obtained by extrapolation assuming the linearity of the $\ln k$ *vs.* $1/T$ plot and the $\ln a$ *vs.* $1/T$ plot, respectively.

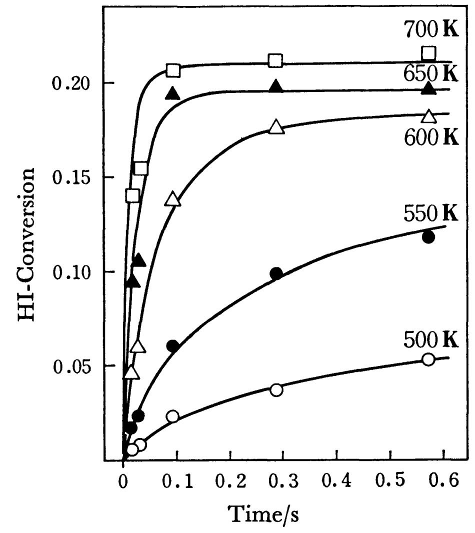


Fig. 2. Contact time-conversion relationship of hydrogen iodide over the Pt/C catalyst.

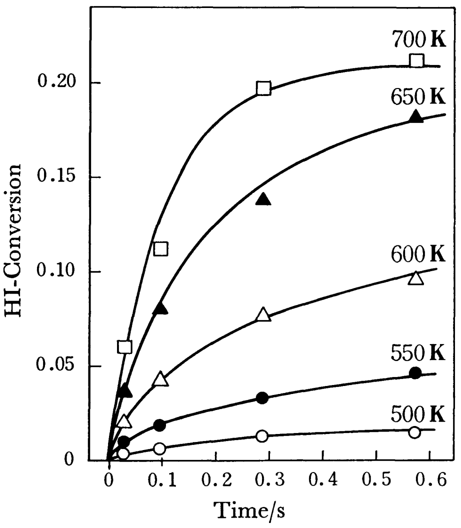


Fig. 3. Contact time-conversion relationship of hydrogen iodide over the active carbon catalyst.

of k and a are presented in Table 2. The continuous curves in Figs. 2 and 3 are obtained by employing Eq. 19 along with the k and a in Table 2. Because the equilibrium conversions of hydrogen iodide at temperatures of 600 K, 650 K, or 700 K in the presence of water vapor differed little from the values calculated by employing the free-energy changes cited from the JANAF Thermochemical Tables,[12)] as will be explained in the section on the "Influence of the Partial Pressure of Water Vapor," the authors adopted the latter for x_e at each temperature from 500 K to 700 K for simulation by the use of Eq. 19. The continuous curves in Figs. 2 and 3 simulate the experimental data fairly well, supporting the conclusion that the assumed reaction scheme is comparatively appropriate.

Influence of the Partial Pressure of Hydrogen Iodide. For the rate equation at the initial stage, Eq. 20 is obtained by substituting zero for x in Eq. 8:

$$v = \frac{P\mathrm{d}x}{\mathrm{d}t} = \frac{k_f K_{HI} P}{1 + K_{H_2O}P_{H_2O} + K_{HI}P}. \tag{20}$$

Equation 20 is transformed to Eq. 21:

$$\frac{v}{P} = \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_f K_{HI}}{1 + K_{H_2O}P_{H_2O} + K_{HI}P}. \tag{21}$$

It is reasonable to regard the data at 500 K, 550 K, and 600 K at a contact time of 1.43×10^{-2} s in Fig. 2 as those for the initial stage of the reaction. The conversion obtained when P, P_{H_2O}, and P_{Ar} were equal to 0.0761 atm, 0.415 atm, and 0.509 atm respectively at a contact time of 1.43×10^{-2} s were 0.00521 (500 K), 0.0159 (550 K), and 0.0444 (600 K). These values differ little from those shown in Fig. 2, for which the following partial pressures were used: P (0.125 atm), P_{H_2O} (0.682 atm), and P_{Ar} (0.193 atm). From these results, it is concluded that both $K_{H_2O}P_{H_2O}$ and $K_{HI}P$ are negligibly small compared to 1 in this range of their partial pressure by considering the form of Eq. 21, as $k_f K_{HI}$ remains constant.

Influence of the Partial Pressure of Water Vapor. The polarity of hydrogen iodide is strong. However, the polarities of hydrogen and iodine, the decomposition products of hydrogen iodide are weak. Therefore, there is the possibility that only hydrogen iodide is stabilyzed by the interaction with water vapor and that the conversion of hydrogen iodide decreases in the presence of water. The influence of the coexistence of water vapor on the equilibrium conversion of hydrogen iodide is small, as is shown by a comparison of the experimental conversions corresponding to that at the long contact time at 600—700 K in Fig. 2 with the calculated equilibrium conversions presented in Table 2.

When water vapor is added to the vapor of hydriodic acid, the rate equation at the initial stage is expressed as follows, on the basis of Eq. 20, where P_{H_2O} is the partial pressure of the water vapor including the added

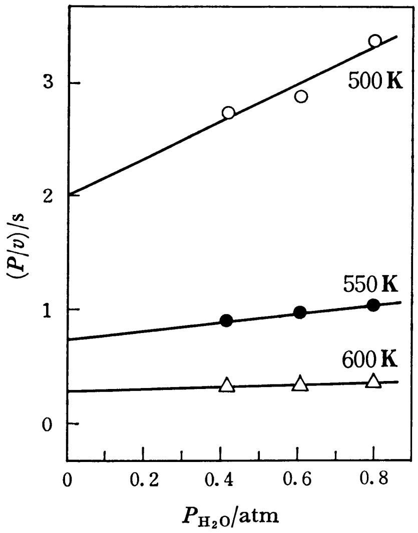


Fig. 4. Effect of water vapor addition on the initial rate of the decomposition of hydrogen iodide over the Pt/C catalyst (0.086 g): P=0.0761 atm, P_{H_2O}= 0.415, 0.605, and 0.795 atm, P_{Ar}=balance.

water vapor:

$$v = \frac{P\,dx}{dt} = \frac{k_f K_{HI} P}{1+K_{H_2O}P_{H_2O}+K_{HI}P}. \qquad (22)$$

The transformation of Eq. 22 yields Eq. 23:

$$\frac{P}{v} = \frac{1}{\frac{dx}{dt}} = \frac{1+K_{HI}P}{k_f K_{HI}} + \frac{K_{H_2O}P_{H_2O}}{k_f K_{HI}}. \qquad (23)$$

It is shown in Eq. 23 that the plot of 1/(dx/dt) against the partial pressure of water vapor gives a straight line and that the intercept of the extrapolated line at the partial pressure zero is the reciprocal of (dx/dt) in the absence of water vapor. The experimental results are depicted in Fig. 4. If the extrapolation of the straight line is significant even in the range where the partial pressure of water vapor is small or near zero, it can be said that the reaction rate of the decomposition of hydrogen iodide in the presence of water vapor does not differ so much from that in its absence.

Influence of the Partial Pressure of Iodine. Figure 5 shows the calculated values of the equilibrium conversion of hydrogen iodide in the presence of iodine in the gas phase added in advance of the decomposition. Calculation was carried out according to the following equation, where K is the equilibrium constant for the decomposition of hydrogen iodide, m is the ratio of the pressure of iodine added in advance of the decomposition to that of hydrogen iodide, and x is the conversion of hydrogen iodide:

$$K = \frac{\sqrt{x(x+2m)}}{2(1-x)}.$$

It can be seen from Fig. 5 that the coexistence of iodine in the gas phase lowers the equilibrium conversion of hydrogen iodide remarkably.

When iodine is added to hydriodic acid, the rate equation at the initial stage of the reaction is expressed as follows on the basis of Eq. 20, where $P^\circ_{I_2}$ is the partial pressure of the added iodine:

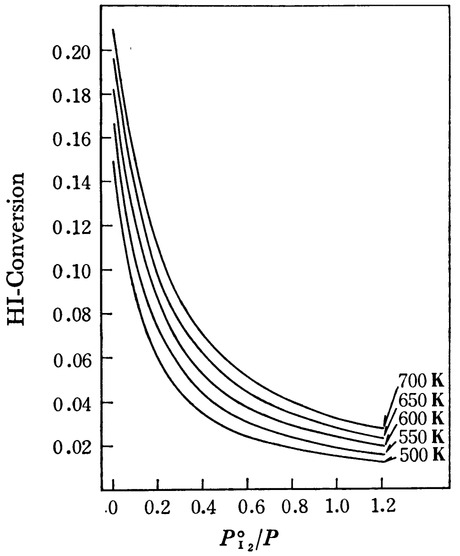


Fig. 5. Dependence of the equilibrium conversion of hydrogen iodide on the ratio of the pressure of iodine present in advance of the reaction ($P^\circ_{I_2}$) to the initial pressure of hydrogen iodide (P).

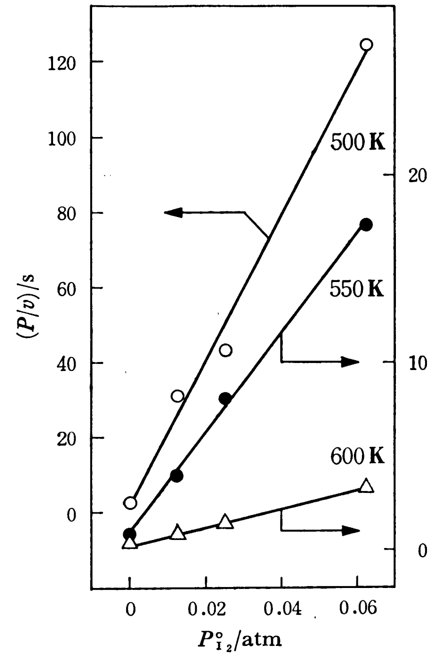


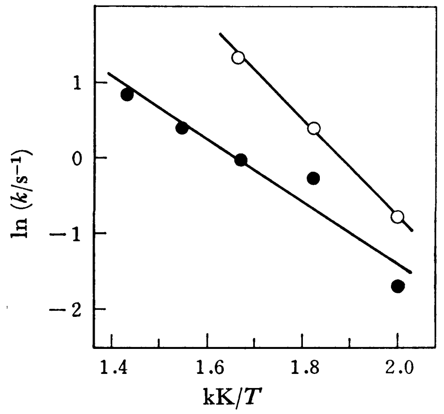
Fig. 6. Effect of iodine addition on the initial rate of the decomposition of hydrogen iodide over the Pt/C catalyst (0.086 g): P=0.125 atm, P_{H_2O}=0.682 atm, $P^\circ_{I_2}$=0, 0.0125, 0.0250, and 0.0625 atm, P_{Ar}=balance.

$$v = \frac{P\,dx}{dt} = \frac{k_f K_{HI} P}{1+K_{H_2O}P_{H_2O}+K_{HI}P+K_{I_2}P^\circ_{I_2}}. \qquad (25)$$

The transformation of Eq. 25 yields Eq. 26:

$$\frac{P}{v} = \frac{dt}{dx} = \frac{1+K_{H_2O}P_{H_2O}+K_{HI}P}{k_f K_{HI}} + \frac{K_{I_2}P^\circ_{I_2}}{k_f K_{HI}}. \qquad (26)$$

Therefore, the plot of 1/(dx/dt) against the partial pressure of iodine gives a straight line, and the intercept at the zero pressure, the reciprocal of (dx/dt) in the absence of iodine. The experimental results



Fif. 7. Arrhenius plots for the decomposition of hydrogen iodide over the Pt/C catalyst and active carbon catalyst.
○: Pt/C catalyst, ●: active carbon catalyst.

are shown in Fig. 6. It is notable that the reaction rate at the initial stage decreased remarkably with the addition of iodine in the low-temperature range. For example, the reaction rate at the initial stage in the presence of 0.0625 atm ($P_{HI}/P^{\circ}_{I_2}=2$) of iodine was about a fiftieth of that in the absence of iodine at 500 K.

Activation Energy and Heat of Adsorption. As has been described above, k and a are expressed as follows:

$$k = \frac{k_f K_{HI}}{1+K_{H_2O}P_{H_2O}+K_{HI}P} \tag{10}$$

$$a = \frac{(K_{H_2}/2+K_{I_2}/2-K_{HI})P}{1+K_{H_2O}P_{H_2O}+K_{HI}P}. \tag{11}$$

As has been mentioned above, $K_{H_2O}P_{H_2O}$ and $K_{HI}P$ are negligible compared to 1 under the present experimental conditions. Therefore, Eqs. 10 and 11 are transformed to give the following equations:

$$k \approx k_f K_{HI} \tag{27}$$

$$a \approx (k_{H_2}/2+K_{I_2}/2-K_{HI})P. \tag{28}$$

Equation 27 shows that k is nearly equal to the apparent rate constant of the decomposition reaction of hydrogen iodide on the catalyst surface. Figure 7 shows the plot of ln k *vs.* $1/T$; the straight line in the figure was obtained by the treatment of least-squares fitting. From Fig. 7, the apparent activation energy of the decomposition of hydrogen iodide was given as 12.7 kcal/mol over the Pt/C catalyst and as 8.21 kcal/mol over the active carbon catalyst. The value obtained over the Pt/C catalyst is near to that obtained over the Pt wire by Hinshelwood and Burk$^{7)}$ (14 kcal/mol).

K_{H_2}, K_{I_2}, and K_{HI} in Eq. 28 are expressed as follows by the use of the heats of adsorption of the corresponding chemical species:

$$\begin{aligned} K_{H_2} &= \exp(-\Delta G^{\circ}_{H_2}/RT) = \exp(\Delta S^{\circ}_{H_2}/R)\cdot\exp(-\Delta H^{\circ}_{H_2}/RT) \\ &= c_1\cdot\exp(q(H_2)/RT) \\ K_{I_2} &= c_2\cdot\exp(q(I_2)/RT) \\ K_{HI} &= c_3\cdot\exp(q(HI)/RT), \end{aligned} \tag{29}$$

where $\Delta G^{\circ}_{H_2}$, $\Delta S^{\circ}_{H_2}$, $\Delta H^{\circ}_{H_2}$, and $q(H_2)$ are the standard Gibbs free energy change, the standard entropy change, the standard enthalpy change of adsorption of hydrogen, and the heat of adsorption of hydrogen, respectively. The other symbols are defined as above. By substituting Eq. 29 in Eq. 28, Eq. 30 is obtained:

$$\begin{aligned} a = (&c_1\cdot\exp(q(H_2)/RT)/2 + c_2\cdot\exp(q(I_2)/RT)/2 \\ &- c_3\cdot\exp(q(HI)/RT))P. \end{aligned} \tag{30}$$

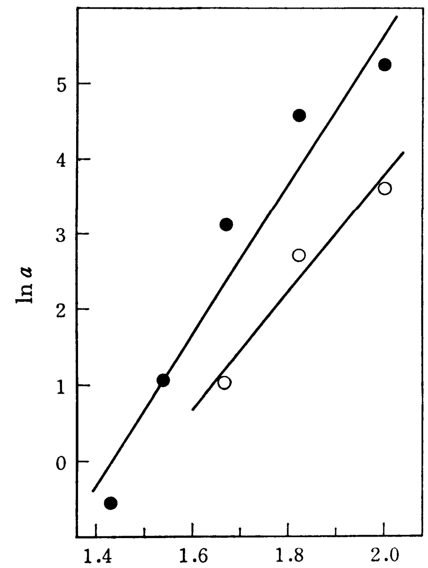


Fig. 8. Relations between the reciprocal of T and ln a.
○: Pt/C catalyst, ●: active carbon catalyst.

The values of $q(H_2)$ and q(HI) on the active carbon have been reported in the literature: $q(H_2)$ is 2.5 kcal/mol$^{13)}$ and q(HI) is 21—23$^{14)}$ kcal/mol. As is shown in Table 2, the values of a on the active carbon are positive, and when ln a is plotted against $1/T$ on a straight line by the least-squares fitting, the slope of the line is positive and big as is shown in Fig. 8. Therefore, none of the terms except for $c_2\cdot\exp(q(I_2)/RT)/2$ are considered to be dominant in Eq. 30. On the basis of this discussion, the following equation is obtained:

$$\ln a \approx q(I_2)/RT + \ln(c_2\cdot P/2). \tag{31}$$

Equation 31 means that, when ln a is plotted against $1/T$ on a straight line, the slope of the line gives $q(I_2)/R$. The value of $q(I_2)$ on the active carbon has not yet been reported. However, it may be estimated as follows:

$$q(I_2) = 2q(C_2H_5I) - q(n\text{-}C_4H_{10}),$$

where $q(C_2H_5I)$ and $q(\text{n-}C_4H_{10})$ are the heat of adsorption of ethyl iodide and butane on an active carbon, as reported in Ref. 13. The value of $q(I_2)$, 16.4 kcal/mol, is obtained by the use of the values of $q(C_2H_5I)$, 14.0 kcal/mol, and $q(\text{n-}C_4H_{10})$, 11.6 kcal/mol. The estimated value of $q(I_2)$ on the active carbon is comparable to that obtained from the slope of the ln a *vs.* $1/T$ plot of the active carbon catalyst (20.7 kcal/mol). This fact also supports the validity of the kinetic analysis employed in the present research.

The results obtained in the present research may be summarized as follows: 1) The contact time-conversion relationship of the catalytic decomposition of hydrogen iodide over the Pt/C catalyst and the active carbon catalyst was simulated successfully by the use of a rate equation derived from an assumed reaction scheme. 2) The influence of water vapor on the rate and equilibrium of the decomposition of hydrogen iodide was small. 3) The Pt/C catalyst and the active carbon catalyst were consumed through the water-gas reaction in the high-temperature range (above 700 K for the former catalyst and above 800 K for the latter). 4) The presence of iodine in the gas phase in advance of the decomposition of hydrogen iodide lowers its equilibrium conversion remarkably, as judged on the basis of a thermodynamic calculation. 5) The inhibition effect of iodine on the rate of the catalytic decomposition of hydrogen iodide over the Pt/C catalyst was remarkable below 550 K.

On the basis of these results, the present authors have concluded that the Pt/C catalyst and the active carbon catalyst should be used in the temperature range of 550—700 K, where the water-gas reaction is almost negligible and where the inhibition effect of iodine is small. For the catalytic decomposition of hydrogen iodide in the lower temperature range, the development of a catalyst which suffers little inhibition effect from iodine is required, or the decomposition should be carried out in combination with a separation method that can continuously remove the iodine formed in the gas phase, even in the presence of water.

The authors wish to thank Drs. Naoyuki Todo, Kenzo Fukuda, and Etsuo Akiba for their valuable discussions. We also would like to thank Mr. Eiji Miyazawa for his cooperation in the experiment and Mr. Atsushi Kinase for his cooperation in several calculations.

References

1) J. H. Norman, K. J. Mysels, D. R. O'Keefe, S. A. Stowell, and D. G. Williamson, Proceedings of the 2nd World Hydrogen Energy Conference (WHEC), Zürich, 513 (1978).

2) M. Dokiya, K. Fukuda, T. Kameyama, Y. Kotera, and S. Asakura, *Denki Kagaku*, **45**, 139 (1977).

3) G. De Beni, G. Pierini, G. Spelta, D. van Velzen, and H. Langenkamp, Proceedings of the 2nd WHEC, Zürich 617 (1978).

4) T. Ohta, N. Kamiya, and M. Yamaguchi, *Int. J. Hydrogen Energy*, **3**, 203 (1978).

5) W. Kondo, S. Mizuta, T. Kumagai, Y. Oosawa, Y. Takemori, and K. Fujii, Proceedings of the 2nd WHEC, Zürich, 909 (1978).

6) Y. Oosawa, Y. Takemori, and K. Fujii, *Nippon Kagaku Kaishi*, **1980**, 1081.

7) C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 2896 (1925).

8) I. Iida, *Z. Phys. Chem. Neue Folge*, **109**, 221 (1978).

9) O. Levenspiel, "Chemical Reaction Engineering," John Wiley & Sons, New York (1962), Chap. 6.

10) O. Levenspiel and K. B. Bishoff, *Ind. Eng. Chem.*, **53**, 313 (1961).

11) "Shokubai Chosei Oyobi Shikenho," ed by Y. Ogino, Chijin Shokan, Tokyo (1965), p. 293.

12) "JANAF Thermochemical Tables," Dow Chemical Company, Midland (1977).

13) "Landolt Börnstein Tabellen," 6 Aufl., II Band, 4 Teil, "Kalorische Zustandsgrössen," Springer Verlag, Berlin (1961).

14) C. L. Mantell, "Industrial Carbon," D. van Nostrand Company, New York (1946).