# STUDIES ON THE KINETICS OF THE GAS-PHASE ADDITION REACTION

OF HI TO BUTADIENE II

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The kinetics of the gas-phase addition reaction of HI to butadiene has been studied from 190° to 230°C using a spectrophotometric apparatus to follow I_2 production. This reaction proceeds homogeneously and quantitatively to yield butene and I_2 in accordance with the equation

$$\text{butadiene} + 2HI \longrightarrow \text{butene} + I_2.$$
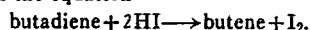
The rate determining step of this addition reaction is

$$C_4H_6 + HI \longrightarrow C_4H_7I.$$
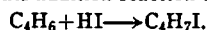
The second-order rate constant, k_1 (l/mole-sec), is given by

$$\log k_1 = 9.04 - 19.2/4.575\,T.$$

The reaction was also examined under the existence of argon gas, and it was found to be the same as the butadiene—HI system. The second-order rate constant, k_1', is given by

$$\log k_1' = 6.57 - 13.9/4.575\,T.$$

The addition of HI occurs at one double bond of butadiene and it produces butene-1 as a final product.

Introduction

The addition of HI to butadiene (C_4H_6) seems to consist of two consecutive stages: the first is a reversible addition reaction to form butene iodide and the second the exchange reaction of the iodide with HI to form butene and I_2.

$$C_4H_6 + HI \rightleftharpoons C_4H_7I \qquad , \qquad\qquad (1)$$

$$C_4H_7I + HI \rightleftharpoons C_4H_8 + I_2 \quad . \qquad\qquad (2)$$

As the rate of the exchange reaction (2) is very fast, as mentioned in the previous paper[1], reaction (1) and (2) cannot be considered separately but the total reaction is observed as follows,

$$C_4H_6 + 2HI \rightleftharpoons C_4H_8 + I_2 \quad .$$
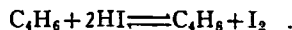
HI and I_2 having a large optical absorption coefficient the concentration of these gases can be measured by the change of the absorption with precision of 0.1 mmHg. In the previous experiment, the addition reaction of HI to butadiene was examined kinetically using the concentration of HI and it was concluded that reaction (1) is a rate determining. The rate constant (l/mole-sec), then, is as follows.

1) H. Kubota, *This Journal*, **37**, 25 (1967)

$$\log k = 8.59 - 18.31/4.575\,T \quad .$$

Here the change of the I_2 concentration in the reaction products is measured photometrically. Using the I_2 concentration measured, the rate constant, k, reported previously, was examined from the construction of more detailed mechanism. The addition reaction of HI to butadiene with argon was also discussed. It is very interesting to know what effect is produced by adding argon on the rate constant, on the kind of reaction products and on the reaction mechanisms of the addition reaction.

Experimentals

Materials

Gaseous hydrogen iodide and butadiene were prepared and stored by the same method as used in the previous work. The solidified HI at the temperature of liquid nitrogen was always white solid, but slight yellow coloring was sometimes observed most likely due to I_2. The trap containing HI was always kept at a dryice-alcohol bath to prevent any I_2 from escaping into the reaction vessel. Argon gas, 99.999% purity, was used in the experiment without any further purification.

Experimental procedures and results

The experimental apparatus were the same as those used in the previous work, but in this work monochromator was used instead of an interference filter. The concentration of I_2 was measured by the use of this monochromator. A schematic diagram of the apparatus is shown in Fig. 1. The change of I_2 concentration was measured at the wave length of $450\,m\mu$ and $470\,m\mu$. The plots of the change of I_2 concentration against the reaction time are shown in Fig. 2. The experimental procedure is the
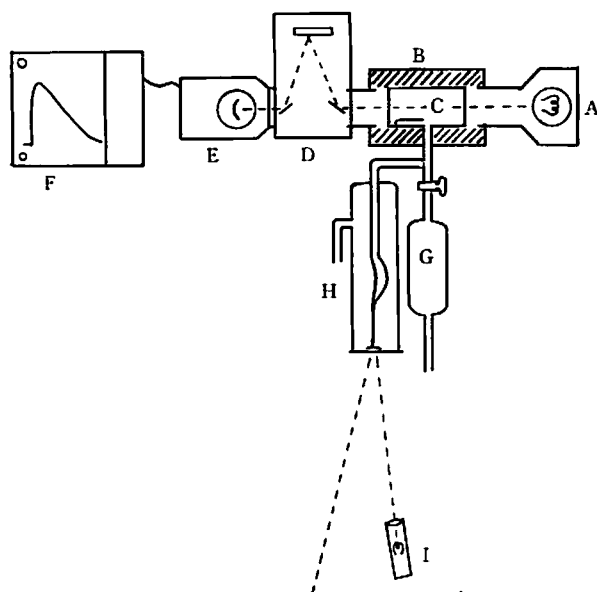

Fig. 1   Schematic diagram of the reaction
apparatus
A : lamp
B : furnace
C : reaction vessel
D : monochromator
E : photomultiplier
F : recorder
G : mixing vessel
H : spoon gauge
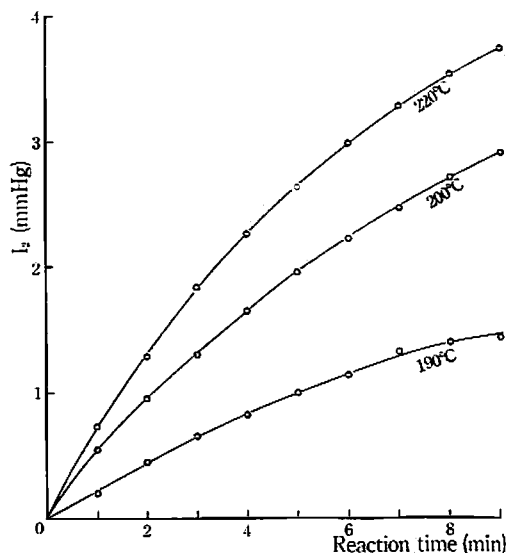I : lamp scale

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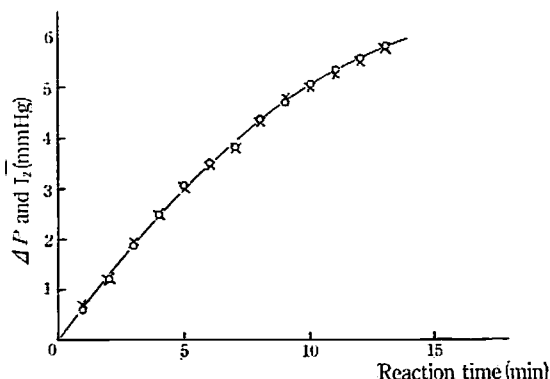Fig. 2   Typical spectrophotometric record of
         I_2 pressure

Fig. 3   Plots of the I_2 pressure and of the total
         pressure *vs.* reaciton time
         $\bigcirc$: I_2, $\times$: ΔP=(total pressure)$_0$
         $-$(total pressure)$_t$
         Experimental conditions
         Reaction temperature 200°C
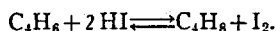   Initial HI pressure 25.4 mmHg
         Initial C_4H_6 pressure 13.2 mmHg

same as that described in the previous report, but is slightly changed when argon is added. At first a purified gas of HI was introduced into the reaction vessel until a desired pressure was reached. The reaction vessel was cut off from the rest of the apparatus and after the removal of residual HI (by condensing in a liquid nitrogen trap and separating this trap with the stopcock) in the apparatus, the whole system was evacuated to high vacuum (10^{-5}mmHg).

Butadiene and argon were introduced in a mixing vessel at a desired composition and at a pressure sufficiently higher than that of HI in the reaction vessel to prevent the backflow of HI on connecting the two vessels. This gas mixture was let in by sudden opening and closing of the stopcock connecting the two vessels. The whole procedures were carried out in a dark room to prevent the decomposition of HI by light and in the vacuum of 10^{-5}mmHg to prevent decomposition of HI and the polymerization of butadiene by oxygen. The Reactions were carried out in the temperature range of 190°~230°C and at various reaction time from 1 to 40 minutes. The base line of the recorder was rechecked to see if any drift had occurred during the course of a reaction. This was a rare occurrence and was not observed in the runs, the results of which are reported here. The change of the I_2 concentration was used to follow the reaction. The following steps can be taken for the formation of I_2 :

$$C_4H_6 + HI \rightleftharpoons C_4H_7I \qquad , \qquad\qquad (1)$$

$$C_4H_7I + HI \rightleftharpoons C_4H_8 + I_2 \quad , \qquad\qquad (2)$$

the over-all reaction being

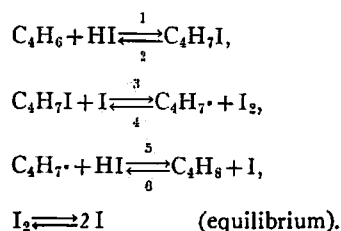$$C_4H_6 + 2\,HI \rightleftharpoons C_4H_8 + I_2.$$

In view of these reaction mechanisms and the experimental result that, as shown in Fig. 3, the decrease of the total pressure is equal to the increase of I_2 concentration, the following relations are used to compute the concentrations of butadiene, hydrogen iodide and iodine:

$$(C_4H_6)_t = (C_4H_6)_0 - (I_2)_t,$$
$$(HI)_t = (HI)_0 - 2(I_2)_t, \qquad\qquad (3)$$
$$2(I_2)_t = (HI)_0 - (HI)_t.$$

Results

The addition reaction of HI to butadiene

The present measurements were carried out in the temperature range of $190° \sim 230°C$ with the mixtures of different composition of butadiene and HI and at different reaction time from 1 to 40 minutes. Analysis of the products by means of a gas chromatography (dimethylsulfolane column) show the existence of butene-1, *trans*-butene-2, *cis*-butene-2 and of small amounts of *n*-butane. In the range of low reaction temperature, a very small amount of polymer which was considered to be a dimer or a trimer of butadiene was obtained. As for the *n*-butane, it seems that the butenes produced by this reaction do not react with HI in this experimental temperature range. In order to confirm this presumption, pure butene-1 or butene-2 was reacted with HI in the temperature range $200° \sim 250°C$ but the reaction did not proceed and the formation of *n*-butane was very little. So small an amount of the *n*-butane produced need not take account stoichiometrically. The polymer of butadiene remained after the reaction products were condensed by a liquid nitrogen trap and evaporated into a sampling vessel for gas chromatographic analysis. This polymer vanished when it was evacuated at room temperature. The reaction mechanisms (1) and (2), mentioned above, are considered to be separated into detailed reaction mechanisms which are constructed by the following steps,

$$C_4H_6 + HI \underset{2}{\overset{1}{\rightleftharpoons}} C_4H_7I,$$

$$C_4H_7I + I \underset{4}{\overset{3}{\rightleftharpoons}} C_4H_7\cdot + I_2,$$

$$C_4H_7\cdot + HI \underset{6}{\overset{5}{\rightleftharpoons}} C_4H_8 + I,$$

$$I_2 \rightleftharpoons 2\,I \qquad \text{(equilibrium)}.$$

It is not clear whether the value of k as reported previously corresponds to k_1 or k_3 of the reaction mechanism mentioned above. Then, on the assumption that the rate determining step is the second order reaction having the rate constant k_1, the above scheme gives the following rate equation using steady state assumption. The concentrations of HI and butadiene were calculated using equation (3).

$$\frac{d(I_2)}{dt} = \frac{k_1 k_3 k_5 (C_4H_6) K_{I_2}^{1/2} (I_2)^{1/2} (HI)}{k_2 k_4 (I_2)/(HI) + k_2 k_5 + k_3 k_5 K_{I_2}^{1/2} (I_2)^{1/2}} \cdot$$

The alternative form,

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$$\frac{(C_4H_6)(HI)(I_2)^{1/2}}{d(I_2)/dt}=\frac{k_2}{k_1k_3K_{I_2}^{1/2}}\left[1+\frac{k_4(I_2)}{k_5(HI)}\right]+\frac{(I_2)^{1/2}}{k_1} , \qquad (4)$$

where K_{I_2} is the equilibrium constant for iodine atom formation. In the early stage of the reaction, it is $(HI) \rangle (I_2)$, so if the value of k_4/k_5 is not so large

$$\frac{k_4(I_2)}{k_5(HI)} \doteqdot 0,$$

and equation (4) can be written as

$$Z\equiv\frac{(C_4H_6)(HI)(I_2)^{1/2} \cdot}{d(I_2)/dt}=\frac{k_2}{k_1k_3K_{I_2}^{1/2}}+\frac{(I_2)^{1/2}}{k_1} . \qquad (5)$$

The concentrations of HI and butadiene are obtained from equation (3). Using these values and (I_2), Z can be plotted against $(I_2)^{1/2}$. The plot obtained is shown in Fig. 4 in a full line. In the early reaction stage and within the limits of the approximation, the plot of Z against $(I_2)^{1/2}$ should give a straight
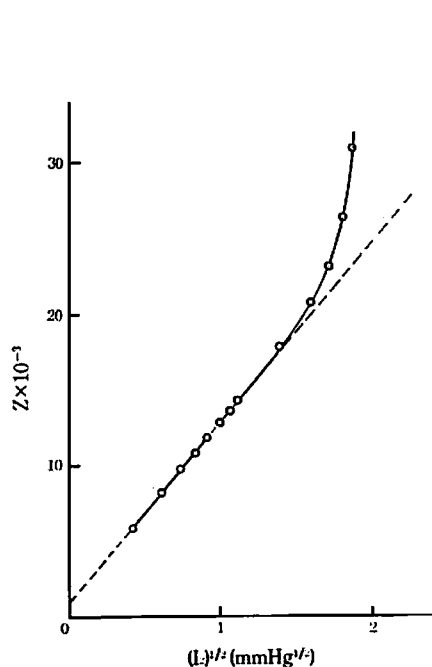

Fig. 4 Plot of the function Z against $(I_2)^{1/2}$
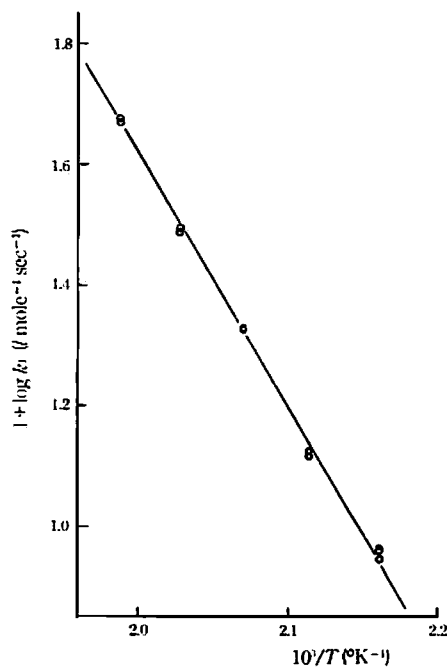Dashed line is extrapolated from early point.
Data for 220°C

Fig. 5 Arrhenius plot of the second-order rate constant

line which is shown as a dashed line in Fig. 4. From the reciprocal of the slope of this dashed line, the value of k_1 is obtained. In Table 1 are listed the values of k_1. As these values agree with those obtained in the previous work, it is clear that the rate determining step of the addition reaction of HI to butadiene is a step having the rate constant k_1. Fig. 5 depicts the Arrhenius plot of k_1 (l/mole-sec) which is best described by

$$\log k_1=9.04-19.2/4.575 T.$$

Table 1   Second-order rate constants at different temperatures and pressures

| Temp. (°C) | Initial pressure (mmHg) | | k_1 |
	[HI]$_0$	[C$_4$H$_6$]$_0$	(l/mole-sec)
190	21.3	14.3	0.911
	9.0	16.6	0.909
	16.7	24.3	0.915
	10.8	10.8	0.885
200	15.9	12.3	1.327
	24.9	10.6	1.318
	13.8	13.3	1.316
	21.0	14.5	1.331
210	10.2	19.4	2.118
	12.6	14.3	2.107
	25.3	8.4	2.133
	14.8	9.4	2.266
220	13.0	5.8	3.185
	24.0	15.0	3.118
	20.0	11.3	3.121
	9.7	15.8	3.127
230	9.9	12.8	4.759
	8.8	10.5	4.731
	11.3	8.1	4.796
	14.0	10.9	4.818

Previously, the value k_4/k_5 was assumed to be not so large when the rate equation (4) changes into equation (5). Now equation (4) is represented as

$$\frac{(C_4H_6)(HI)(I_2)^{1/2}}{d(I_2)/dt} = \frac{(I_2)}{(HI)} \cdot a + b + (I_2)^{1/2} \cdot c.$$
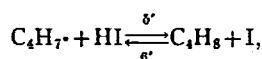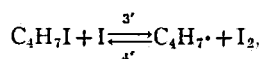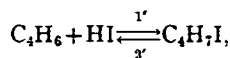
Here $a = \frac{k_2 k_4}{k_1 k_3 k_5 K_{I_2}^{1/2}}$, $b = \frac{k_2}{k_1 k_3 K_{I_2}^{1/2}}$ and $c = \frac{1}{k_1}$. At the constant temperature, the rate constants and the equilibrium constant must be constant, so the values of a, b and c are constant. Since $(I_2)^{1/2}$, $(I_2)/(HI)$ and Z can be calculated from the data, the values of a and b can be determined from any two points on the curve of Z plotted against $(I_2)/(HI)$. The values of k_4/k_5 are determined from a and listed in Table 2.

Table 2   The values of a, b and k_4/k_5

| Temp. °K | Initial pressure (mmHg) | | | | k_4/k_5 |
	[C$_4$H$_6$]$_0$	[HI]$_0$	$a \times 10^{-4}$	$b \times 10^{-3}$	
463	16.6	9.0	18.42	7.72	23.86
	23.9	18.3	18.00	6.64	27.10
					avg. 25.48
503	10.9	14.0	3.19	2.31	18.76
	11.6	11.7	1.70	1.70	16.93
					avg. 17.84

The effect of the inert gas, "Argon"

Considering that the reaction mechanisms of the addition reaction of HI to butadiene in the presence of argon are the same as that mentioned above, the following reaction steps were obtained.

$$C_4H_6 + HI \underset{2'}{\overset{1'}{\rightleftharpoons}} C_4H_7I,$$

$$C_4H_7I + I \underset{4'}{\overset{3'}{\rightleftharpoons}} C_4H_7\cdot + I_2,$$

$$C_4H_7\cdot + HI \underset{6'}{\overset{5'}{\rightleftharpoons}} C_4H_8 + I,$$

$$I_2 \rightleftharpoons 2I \qquad \text{(equilibrium)}.$$

Making the same treatment as in the previous case the following rate equation was obtained.

$$Z' \equiv \frac{(C_4H_6)(I_2)^{1/2}(HI)}{d(I_2)/dt} = \frac{k_2'}{k_1'k_3'K_{I_2}^{1/2}} + \frac{(I_2)^{1/2}}{k_1'} \ . \tag{6}$$

Here K_{I_2} is the equilibrium constant for iodine atom formation. The stoichiometric relations among HI, butadiene and I_2 follow equation (3). Using this relation, equation (6) was plotted. Within the limits of the approximation, the plot of Z' against $(I_2)^{1/2}$ should give a straight line at low concentration of I_2. Such a plot is shown in Fig. 6 with the dashed straight line indicating the choice of initial slope. From the reciprocal of the slope of the straight line, the rate constant k_1' is obtained. This k_1' is listed up in Table 3 with its experimental conditions. Fig. 7 depicts the Arrhenius plot of k_1' (l/mole-sec) which is best described by
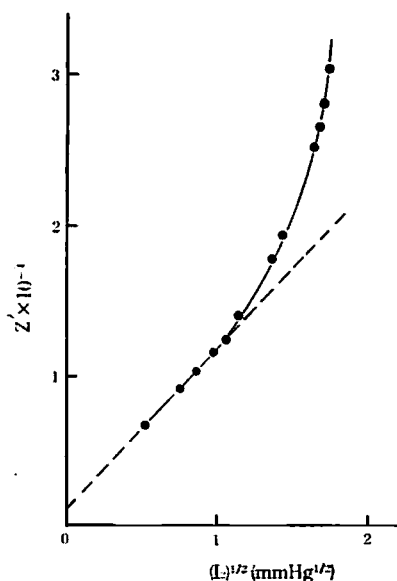
$$\log k_1' = 6.57 - 13.9/4.575\,T.$$

Fig. 6   Plot of the function Z' against $(I_2)^{1/2}$
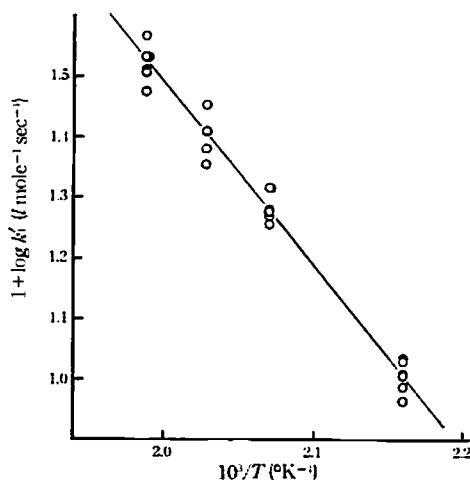   Data for 230°C

Fig. 7   Arrhenius plot of the second-order rate
        constant in the presence of argon

Table 3   Second-order rate constants at different temperatures and pressures in the presence of argon

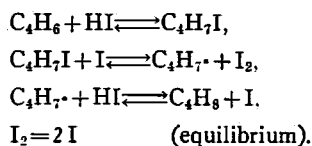| Temp.	Initial pressure (mmHg)			k_1'
°C	$[HI]_0$	$[C_4H_6]_0$	Argon	(l/mole-sec)
	8.0	12.6	14.9	0.924
	17.7	8.9	10.0	1.026
190	14.6	11.3	18.4	1.021
	22.0	2.7	2.5	0.974
	9.3	8.8	8.3	1.085
	17.0	12.6	15.4	1.072
	8.8	10.2	10.1	1.893
	16.0	10.0	10.0	1.802
	16.0	13.0	10.6	1.899
210	9.3	8.8	8.3	1.908
	10.7	8.7	13.9	1.858
	8.5	5.0	21.3	2.071
	12.0	11.6	15.4	2.071
	14.4	8.9	13.5	2.399
	13.1	5.0	7.3	2.399
220	9.1	11.2	10.4	2.258
	13.2	9.7	10.3	2.578
	17.1	10.4	12.6	2.844
	21.8	4.4	8.8	3.407
	10.5	6.5	13.2	2.986
230	10.7	10.2	10.8	3.697
	9.3	6.6	4.2	3.213
	17.0	2.0	1.5	3.404
	10.7	5.8	14.6	3.245

Considerations

Up to date, many elimination reactions[2] of hydrogen iodide from alkyl halide have been studied. These reactions are given such a definition as a four-center reaction where the reaction occurs in a single molecular step. On the other hand, many reverse reactions, such as the addition reaction of hydrogen iodide to olefin, have been studied by many workers[3] but except in the case of HI, attempts have failed.

Many studies of the addition reaction of HI to olefin have been reported by Benson et al[4][5]. They conclude that the addition reactions of HI to olefins are kinetically clean, homogeneous, second-order gas phase reactions and are molecular in nature. In the case of butadiene, from the results of this experiment and of the previous report, the addition reaction of HI to butadiene is considered to consist
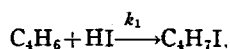
2)   D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, **1951**, 2033
   A. Maccoll and R. H. Stone, *ibid.*, **1961**, 2756
   A. T. Blades and G. W. Murphy, *J. Am. Chem. Soc.*, **74**, 6219 (1952)
   G. Harden, *J. Chem. Soc.*, **1957**, 5024
   J. L. Jones and R. A. Ogg, *J. Am. Chem. Soc.*, **59**, 1939 (1937)
   A. N. Bose and S. W. Benson. *J. Chem. Phys.*, **37**, 2935 (1962)
3)   G. B. Kistiakowsky and C. H. Stauffer, *J. Am. Chem. Soc.*, **59**, 165 (1962)
4)   A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **37**, 1081 (1962)
5)   P. S. Nangia and S. W. Benson, *ibid.*, **41**, 530 (1964)

of such elementary steps:

$$C_4H_6 + HI \rightleftharpoons C_4H_7I,$$

$$C_4H_7I + I \rightleftharpoons C_4H_7\cdot + I_2,$$

$$C_4H_7\cdot + HI \rightleftharpoons C_4H_8 + I,$$

$$I_2 = 2I \qquad \text{(equilibrium)}.$$

The rate determining step is

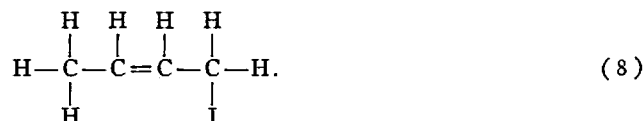$$C_4H_6 + HI \xrightarrow{k_1} C_4H_7I,$$

and the rate constant, k_1 (l/mole-sec), is best described by

$$\log k_1 = 9.04 - 19.2/4.575\,T.$$

The reaction of these two molecules is expressed by the above equation, but the structure of the intermediate, C_4H_7I, is unknown. In this reaction, two structures may be considered as follows. The one is that a HI molecule adds to butadiene following the Markownikoff rule. This is indicated by

$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ H-C-C-C=C-H. \\ | & | \\ H & I \end{array} \qquad (7)$$
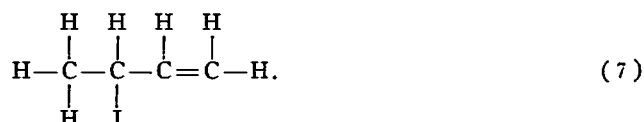
The other is the structure, such as

$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ H-C-C=C-C-H. \\ | & | \\ H & I \end{array} \qquad (8)$$

If the intermediate, C_4H_7I, takes the form (7), butene-1 can be obtained as a reaction product in the initial stage, and if it takes the form (8), butene-2 can be obtained. There exists equilibrium[6]~[9] between butene-1 and butene-2 and its rate is sufficiently rapid in this reaction temperature range. But, from
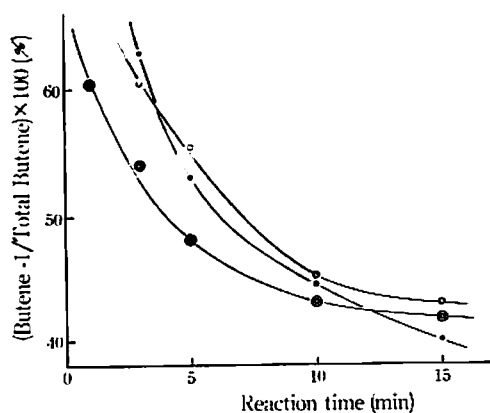

Fig. 8 The ratio of butene-1 to total butene *vs.* reaction time
○: 190°C, ●: 200°C, ◎: 210°C

6) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963)
7) S. W. Benson and A. N. Bose, *ibid.*, **85**, 1388 (1963)
8) D. M. Golder, K. W. Egger and S. W. Benson, *ibid.*, **86**, 5416 (1964)
9) K. W. Egger, D.M. Golden and S. W. Benson, *ibid.*, **86**, 5420 (1964)

Table 4   Energies of activation and the frequency factors for the addition of HI to olefins

Olefin	E (kcal/mole)	log A	literature
C_2H_4	28.9	8.52	2)
C_3H_6	23.4	7.89	4)
i-C_4H_8	18.0	6.50	10)
C_4H_8-2	21.1	6.26	5)
C_4H_6	19.2	9.04	present work

the experimental results shown in Fig. 8, in the early stage of reaction, the amount of butene-1 produced is much greater than that of butene-2, the addition reaction of HI to butadiene seems to take the form (7) as a reaction intermediate and then butene-1 is produced. Butene-1 changes into butene-2 by isomerization.

In Table 4, the data of activation energies and frequency factors for ethylene, propylene, *iso*-butylene, butene-2 reported by Benson *et al.*, and butadiene are listed. From the data of Table 4 it can be considered that α-CH_3 substitution produces a large effect on the rate constant of the addition reaction of HI to olefins. Taking the value of the activation energy of ethylene as the standard, the activation energy decreases about 6 kcal/mole according to the replacement of the hydrogen atom of ethylene by CH_3. Assuming that butadiene is an ordinary conjugated compound, the double bonds of the butadiene are more stable than that of ethylene, so it seems that the activation energy of the addition reaction of HI to butadiene must be larger than that of ethylene. But these experimental results show that the activation energy of butadiene is smaller than that of ethylene. Such behavior is not anticipated in terms of any known ground-state interactions of butadiene with any species of HI in the gas phase. For the reason mentioned above, the vinyl group in butadiene which is not concerned with the addition reaction seems to exert the effect on the addition reaction rate twice as large as CH_3 does.

Changing the standpoint of view, this addition reaction is examined from the standpoint of quantum chemistry whether it is an intermolecular reaction with four-center cyclic structure as an intermediate or it is a reaction of dissociated HI adding to the double bond one by one.

A series of the reports by Woodward and Hoffmann[11] points out that the reactivity of the double bond depends on the symmetry of the molecular orbitals. Using the frontier electron theory by Fukui *et al.*, and the perturbation theory by Dewar[12], it may explain theoretically that the molecular orbitals which control the Woodward-Hoffmann rule are the highest occupied molecular orbital (HO) and the lowest vacant molecular orbital (LV). Considering the case that HI decomposes and adds to the double bond, it may have the orientation that 1·2 addition is trans and 1·4 addition is cis. From the standpoints of the four-center theory by Benson and the cis addition in a wide sense, it may take 1·4 addition and butene-2 should be obtained as reaction products. Thinking the case that HI does not decompose but

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

11)   R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 395, 2046, 2511, 4388 (1965)

12)   R. Hoffmann and R. B. Woodward, *Tetrahedron Letters*, **28**, 2427 (1965)
       K. Fukui, *Bull. Chem. Soc. Japan*, **39**, 498 (1965)

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adds to the double bond as a molecule, (A) in the case that the (LV) of HI is antisymmetry, 1·2 addition is trans and 1·4 addition is cis and butene-2 is obtained as reaction product : (B) in the case that the (LV) of HI is symmetry, clearly 1·2 addition is cis and 1·4 addition is trans. In this case the reaction product is butene-1 and it accords with the experimental result. From the discussion of the standpoint of quantum chemistry as mentioned above, it is doubtful that the addition reaction of HI to butadiene is a four-center reaction.

From the experimental results, the reaction in which the inert gas argon was added to the HI—butadiene system is essentially the same as the reaction of HI—butadiene system and the same treatment is possible concerning the reaction mechanisms and the reaction kinetics. But discrepancy of Z' in equation (6) from the straight line begins with lower I_2 concentration and the values of the rate constants are considerably scattered. The rate constants of this case have small values at high reaction temperature and have equal or large values at low temperature compared with the rate constants of HI—butadiene system. These discrepancies are induced clearly by the addition of inert gas. The change of the frequency factor of this reaction may be considered to be that of the activation entropy. At high temperature, the activation entropy is small and at low temperature, the activation entropy large. If the value of entropy change is sufficiently large enough as compared with the change of reaction temperature, the rate constants decrease at high reaction temperature and increase at low reaction temperature, as the results of this experiment show.

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