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STUDIES ON THE KINETICS OF THE GAS-PHASE ADDITION REACTION OF HI TO BUTADIENE I

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The kinetics of the gas-phase butadiene$+2HI=$butene$+I_2$ has been studied from 180° to 230°C using a photometric procedure. It is shown that the reaction mechanisms of the addition reaction of HI to butadiene consist of the following two steps.

$$C_4H_6+HI \xrightarrow{k} C_4H_7I \qquad \text{(slow)},$$
$$C_4H_7I+HI \longrightarrow C_4H_8+I_2 \qquad \text{(fast)}.$$

The second-order rate constant k is given by (units of l/mole-sec),

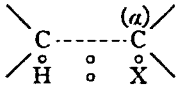
$$\log k = 8.59 - 18.3/4.575\,T.$$

The small activation energy of the addition reaction predicts that the $-CH{=}CH_2$ of butadiene exerts very interesting influence on the addition reaction rate.

Introduction

In the gas-phase reactions, most reactions involve radical pathways and direct molecular reactions seem to be very few. As the molecular reactions are complicated accompanying radical reactions, the reports concerned with the molecular reactions are very rare.

Recently it has been reported1) that the addition reactions of hydrogen halide to olefin occur in a single molecular step, and as an intermediate it has a structure in which four adjacent atoms are sharing their valence electrons in a four-center, cyclic structure of the form,



(Small open circles represent valence electrons.).

Therefore its bonding energy becomes lower and the activation energy of the addition reaction seems to be small compared with the reaction which makes ion pair intermediate. Attempts2) have been made to measure directly the rate of the addition of HCl and HBr to olefins. These have failed because of the temperature range, 200° ~ 500°C, where the equilibrium constant lies wholly on the side of the dissociation so that the addition reaction would be only measurable at concentrations of 10^3 atmospheres or higher.

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1) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 39, 3463 (1963)
2) G. B. Kistiakowsky and C. H. Stauffer, *J. Am. Chem. Soc.*, 59, 165 (1937)

On the other hand, in the addition reaction of HI to olefin, the rate is measurable in this temperature range.

Since 1962, Benson *et al.*, have reported influential studies of propylene³⁾, ethylene⁴⁾, *iso*-butylene⁵⁾ and others⁶⁾. According to their reports, the reaction of olefins with HI consists of two stages. The first is a reversible addition reaction to form alkyl iodide according to the Markownikoff rule and the second is an exchange reaction of the alkyl iodide to form alkane and iodine.

As the second step is too fast, one cannot usually observe the two steps separately but can observe over-all reaction

$$\text{olefin} + 2\,\text{HI} \rightleftharpoons \text{RH}_2 + \text{I}_2.$$

Moreover, all of these reactions have low activation energies and the methyl group which adds to α-carbon atom produces large effect on the addition rate constant. The decrease in activation energy by the replacement of H of the α-carbon atom with CH_3 is about 6 kcal/mole per methyl group¹⁾. Then, it is very interesting to study the addition reaction of HI to the conjugated olefin, for example, butadiene which has two double bonds in it.

Concerning the addition reaction of HI to butadiene, it has not been studied yet whether HI adds to one double bond of butadiene or two double bonds. If the HI addition reaction occurs in one double bond only, what effect is given by the vinyl group which adds to α-carbon atom of butadiene?

Experimentals

Materials

Gaseous hydrogen iodide was prepared by dropping reagent-grade 52 wt% hydriodic acid onto phosphorous pentoxide, in an atmosphere of nitrogen and in the dark room. The liberated gas was allowed to pass through phosphorous pentoxide, a dryice-alcohol trap and finally condensed in a trap cooled with liquid nitrogen.

The gas was further purified by several distillations in vacuum and then finally stored in a flask which was covered with black cloth to prevent photolytic decomposition. Research grade butadiene was dried to pass through Hamond Drielite, sodium hydroxide and silica gel and further purified by distillation in vacuum and finally was stored in a flask. Analysis of a sample of butadiene by gas chromatography on a dimethylsulfolane column did not give any peak for impurities.

Experimental procedure

Kinetic measurements were made in a static method by the use of standard type vacuum line and a photometric system. The schematic diagram of the experimental apparatus was shown in Fig. 1. A is a hydrogen lamp which produces ultra-violet light. B is an electric furnace whose temperature was maintained within ±1°C by an electric controller in conjunction with a thermocouple. C is an inter-

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3) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **37**, 1081 (1962)
4) S. W. Benson and A. N. Bose, *ibid.*, **37**, 2935 (1962)
5) A. N. Bose and S. W. Benson, *ibid.*, **38**, 878 (1963)
6) P. S. Nangia and S. W. Benson, *ibid.*, **41**, 530 (1964)

ference filter ($\lambda_{max}=270\mathrm{m}\mu$, $\Delta\lambda_{\frac{1}{2}}=\pm17\mathrm{m}\mu$). E is a photomultiplier. F is an automatic recorder. G is a gas storage and H is a Bourdon spoon gauge fitted with a lamp and scale, I, having ±0.1 mmHg sensitivity.

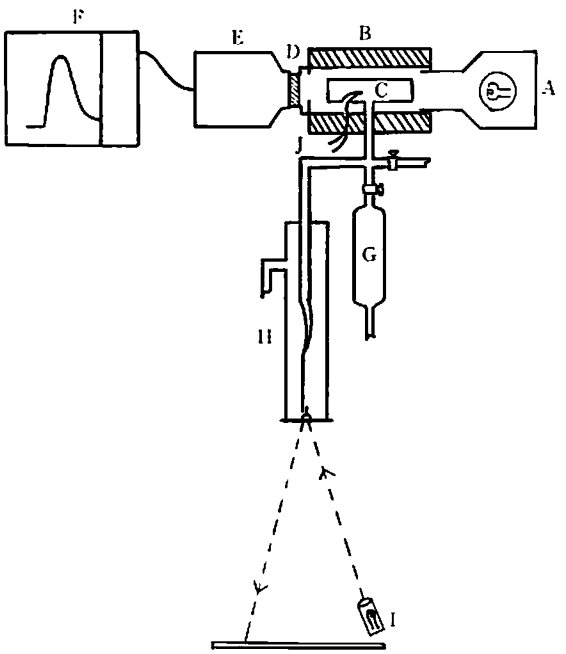

Fig. 1 Schematic diagram of the reaction apparatus
A: lamp
B: furnace
C: reaction vessel
D: filter
E: photomultiplier
F: recorder
G: mixing vessel
H: spoon gauge
I: lamp scale
J: thermocouple

All of the reactions were carried out in a dark room to prevent decomposition of HI by light and in a vacuum of 10^{-5}mmHg to prevent the decomposition of HI and polymerization of butadiene by oxygen. Since iodine has a fairly low vapour pressure, the pipe lines which were connected directly with the reaction vessel were maintained at about 110°C by using tape heater to prevent iodine condensation. Measurements of the pressure change were made by use of the spoon gauge fitted with a lamp and scale. At the same time, the changes of the concentration of HI were recorded on the recorder using an interference filter and a photomultiplier. When HI was let into the vessel alone, it was observed that the pressure decreased by 0.5 mmHg within 1 hour from its addmission, but no further pressure change was observed even if HI was kept in the vessel more than 2 hours. As to the experimental procedure, the purified sample of HI was introduced into the reaction vessel at first. Then, the reaction vessel was cut off from the rest of the apparatus and after the removal of excess HI (by condensing in liquid nitrogen trap and separating this trap with the stopcock) the whole system was evacuated to 10^{-5}mmHg. After starting the automatic recorder, butadiene was introduced in a gas storage at a pressure sufficiently higher than that of HI in the reaction vessel to prevent the backflow of HI on connecting the two vessels. Butadiene was let in by sudden opening and closing of a stopcock connecting the two vessels. After measuring the initial total pressure by spoon gauge, the total pressure change was recorded in a period of 30~60 seconds. After suitable reaction time (1~30 minutes), the reactants and products were allowed to pass through Auramine U tube and ice trap in order to remove the iodine and the residual HI, then finally condensed in a trap cooled with liquid nitrogen. The trapped reaction products were evaporated to the sampling vessel of the gas chromatography and analyzed. 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 whose results are reported here.

Results

The present measurements were carried out in the temperature range 180°~230°C with different composition of butadiene and HI. The analysis of the reaction products besides iodine was carried out by gas chromatography (column: dimethylsulfolane). The reaction products obtained were butene-1, *trans*-butene-2, *cis*-butene-2 and small amount of *n*-butane. From this experimental result that *n*-butane was produced in a small amount, 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°~250°C, but the reaction did not proceed and the formation of *n*-butane was very little. The plots of the total pressure change and of the HI pressure change against the reaction time are shown in Fig. 2. From these plots the amount of the HI consumed is twice as much as the total pressure change.

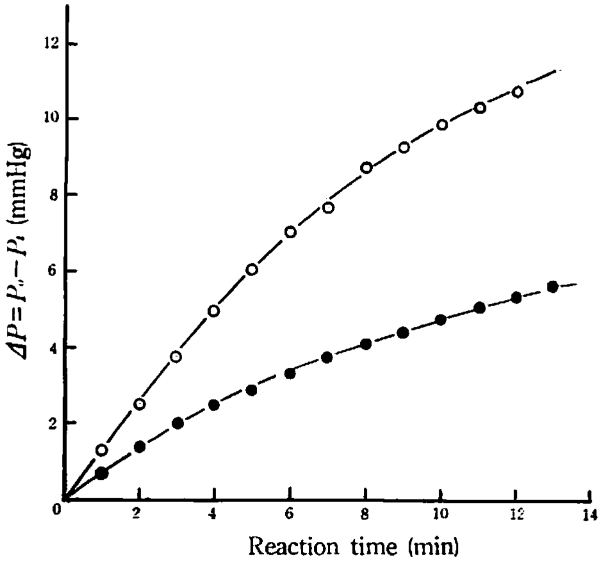

Fig. 2 The plots of the total pressure change and of the HI pressure change against reaction time
Experimental conditions
Reaction temperature: 200°C
Initial HI pressure: 24.9 mmHg
Initial C_4H_6 pressure: 10.6mmHg
○ : HI
● : Total Pressure

Considering the results mentioned above and the kind of the reaction products or the result reported on propylene, *iso*-butylene and others by Benson *et al.*, the reaction mechanisms of the addition reaction of HI to butadiene seems to consist of the following steps,

$$C_4H_6 + HI \rightleftharpoons C_4H_7I, \quad \text{(slow)} \qquad (1)$$

$$C_4H_7I + HI \rightleftharpoons C_4H_8 + I_2 \quad \text{(fast)} \qquad (2)$$

So the over-all reaction can be represented by

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

As the ultra-violet absorption curve of butadiene is overlapped with the part of the absorption curve of the short wave length of HI, the change of the HI concentration was measured by the change of the absorption which does not overlap the absorption of butadiene (measured wave length was 270 mμ). Assuming that the addition reaction of HI to butadiene is second order, the alternative form[7] of the usual second-order rate equation was used to obtain the rate constant. In such a reaction as the following case

$$aA+bB \longrightarrow \text{products},$$

its second-order rate equation can be expressed as

$$-dA/dt=kAB. \qquad (3)$$

If we let $A'=A+\Delta/2$, here $\Delta=(a/b)B_0-A_0$, then equation (3) can be expressed as follows:

$$-dA/dt=(b/a)kA'^2[1-(\Delta/2A')^2].$$

When $\Delta \leq A_0/4$, the term in brackets is

$$1-(\Delta/2A')^2 \geqq 0.99 \qquad : \ t=0,$$

$$1-(\Delta/2A')^2 \geqq 0.96 \qquad : \ t=t_{\frac{1}{2}}.$$

Under these conditions this term is assumed to be constant and is replaced by its average value during the course of the reaction (that is $1-\Delta^2/4A_0'A_f'$). This permits direct integration, giving

$$1/A'-1/A_0'=(b/a)k(1-\Delta^2/4A_0'A_f')t. \qquad (4)$$

The plot of $1/A'$ against t gives a straight line, and by dividing the slope by $(b/a)(1-\Delta^2/4A_0'A_f')$, the second-order rate constant can be obtained with good precision. Now, assuming that A is hydrogen iodide and B is butadiene, the typical plots of $1/A'$ against t are shown in Fig. 3. To obtain the activation energy and the Arrhenius factor, the rate constants were determined from 180°C to 230°C. Table 1 gives the values of the second-order rate constants, k, at different temperatures and the initial pressures

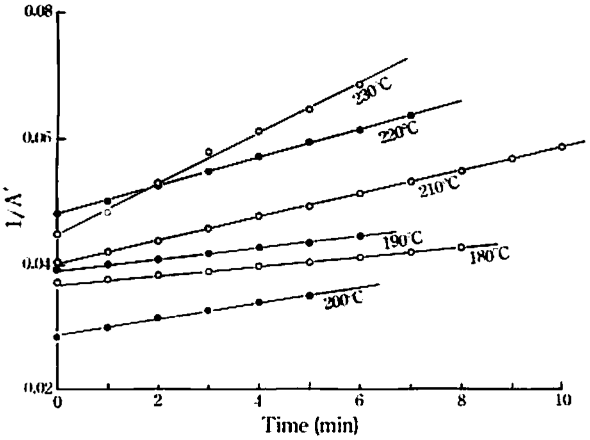

Fig. 3 Typical second-order plots of equation (4)

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[7] S. W. Benson, "The Foundation of Chemical Kinetics", p. 20, McGraw-Hill Book Company, Inc, New York (1960)

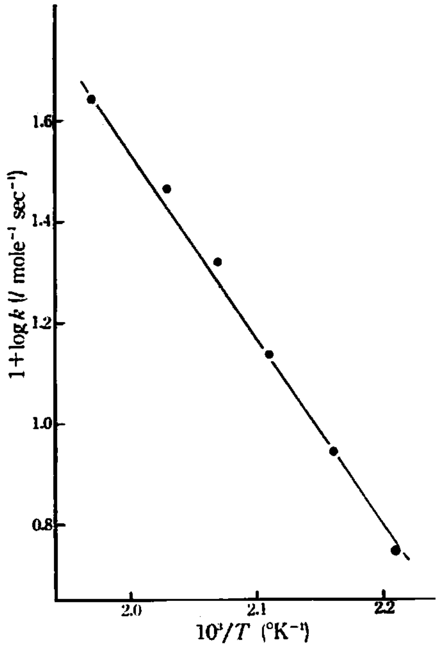

Fig. 4 Arrhenius plot of the second-order rate constant

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

Temp. (°C)	Initial pressure (mmHg) $[HI]_0$	$[C_4H_6]_0$	k (l/mole-sec)
180	28.6	20.4	0.58
	23.8	16.9	0.55
	20.3	10.1	0.49
	29.5	16.5	0.52
190	9.4	13.3	0.86
	18.7	10.7	0.79
	24.0	19.8	0.70
	20.2	21.6	0.73
200	30.1	17.2	1.36
	20.4	10.6	1.40
	22.0	15.6	1.39
	19.8	16.3	1.24
210	22.3	17.2	2.07
	19.2	10.4	2.04
	29.7	10.6	2.03
	9.2	10.5	2.00
220	31.4	20.7	2.87
	27.0	12.1	2.86
	22.3	15.4	2.94
	10.6	11.4	3.04
230	23.7	13.0	4.20
	21.8	10.5	4.67
	22.5	10.3	4.33
	8.6	12.4	4.42

of HI and butadiene as calculated from the plots of the equation (4). Fig. 4 depicts the Arrhenius plot of k (unit of l/mole-sec) which is best described by

$$\log k = 8.59 - 18.3/4.575\,T.$$

Discussion

Judging from such experimental results that butenes and iodine are produced as reaction products, the total pressure change is about half of the decrease of HI pressure and the reaction is satisfied with the second-order rate equation, the addition reaction of HI to butadiene is considered whether one HI molecule adds to one double bond of butadiene to form butene iodide according to the Markownikoff rule or one HI molecule adds to 1·4 carbon atom of butadiene to form 1-iodobutene-2 or these two reactions happen at the same time. The rate of reaction (1) is very slow and so it is assumed that this step will be the rate determining. The reaction intermediate of this rate determining process then will undergo very rapid reaction with HI to form butene-1 or butene-2.

In Table 2, data of activation energies and frequency factors for ethylene, propylene, *iso*-butylene which are reported by Benson *et al.*, and butadiene are listed. From the data of Table 2 it may be understood that α-CH_3 substitution causes a large increase in rate in the addition reaction with a decrease of 5～6 kcal/mole in energy of activation. Comparing with this trend, the vinyl group which is connected with α-carbon atom in butadiene molecule, seems to exert such an influence on the activation energy of the addition reaction of HI to butadiene twice as large as CH_3.

Table 2 Arrhenius parameters for the second-order rate constants

Olefin	E (kcal/mole)	log A	literature
C_2H_4	28.5	8.48	4)
C_3H_6	23.5	7.89	3)
i-C_4H_8	18.1	6.57	5)
C_4H_6	18.3	8.59	present work

The author will mention the details about the addition reaction mechanisms of HI to butadiene in the next report.

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