The Reaction of Hot Deuterium Atoms with *cis*-2-Butene

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(Received December 25, 1973)

The photolysis of deuterium iodide at the wavelength of 2288 Å was carried out in the presence of *cis*-2-butene and iodine at 40 °C. Among the products, hydrogen (D_2 and HD), methane (CH_3D), propylene ($CH_3CH{=}CHD$), *n*-butane ($CH_3CHDCHDCH_3$), and 1-butene were measured as a function of the pressure of *cis*-2-butene. The formation of HD at higher pressures of *cis*-2-butene was attributed to the abstruction of H atoms from *cis*-2-butene-by hot D atoms. This reaction accounted for 8% of the total D atom-reaction. The formations of CH_3D, C_3H_5D, and $C_4H_8D_2$ were well explained by the successive reactions of hot butyl radicals, $C_4H_8D^*$.

In the reaction of recoil-tritium atoms with a saturated hydrocarbon,$^{1)}$ the substitution reaction is well known to occur together with the abstraction reaction:

$$T^* + RH \left\langle \begin{array}{l} \rightarrow RT + H \\ \rightarrow HT + R \end{array} \right.$$

In a previous paper,$^{2)}$ we reported that, when hot deuterium atoms were produced by the photolysis of DI at 2288 Å in the presence of ethylene, a large amount of HD was formed, and that the pressure dependence of this HD formation could be well explained in terms of the following reaction scheme:

$$\begin{tikzcd} D^* + C_2H_4 \arrow[r] & C_2H_4D^* \arrow[r] & H + C_2H_3D \arrow[d, "+DI"] \\ & & HD \end{tikzcd}$$

The so-called "billiard-like" substitution reaction and also the abstraction reaction do not seem to occur with ethylene.$^{3)}$ In the case of propylene, on the other hand, more than 10% of the reaction of hot deuterium atoms is attributable to the abstraction reaction producing HD.

In order to substantiate these findings, we have studied the reaction between hot deuterium atoms and *cis*-2-butene after a slight modification of the reaction system.

Experimental

The deuterium iodide and hydrogen iodide were prepared in a manner described previously.$^{2)}$ The *cis*-2-butene was purchased from the Takachiho Shoji Co., which showed no impurity on gas chromatographic analysis. To keep the reaction system at 40 °C, a small air bath box was made. The temperature inside was kept within ±1 °C by using a modified Beckmann thermometer. The irradiation by a cadmium resonance lamp was performed through a quartz window attached to the box. In each experiment, the cell was saturated with iodine vapor before deuterium iodide and *cis*-2-butene were introduced.

The non-condensable products at 77 K were collected by means of Toepler pump equipped with a cuprous oxide furnace, which was used to combust hydrogen into water when the amount of methane produced was measured. Among the condensable products at 77 K, hydrocarbons were analyzed on the gas chromatograph of a 20-m-long dimethyl sulforane column. The D-content in the product was measured by mass spectrometry after each component had been separated by gas chromatography. Many kinds of alkyl iodides were found to be formed, but they were not analyzed quantitatively.

Results

The photolysis results are summarized in Fig. 1. All the data were obtained when the pressures of DI and I_2 were 10.3 and 1.1 Torr respectively, in a 120-ml reaction vessel; the irradiation time was 6 min. Experiments with HI in place of DI were also carried out. Those results are not shown here, because the curves for each product almost coincided with those for the corresponding products shown in Fig. 1. The plots for HD and D_2 were obtained after a correction was made for the initially-present impurity, HI, in the DI gas. The correction method has been previously described.$^{2)}$

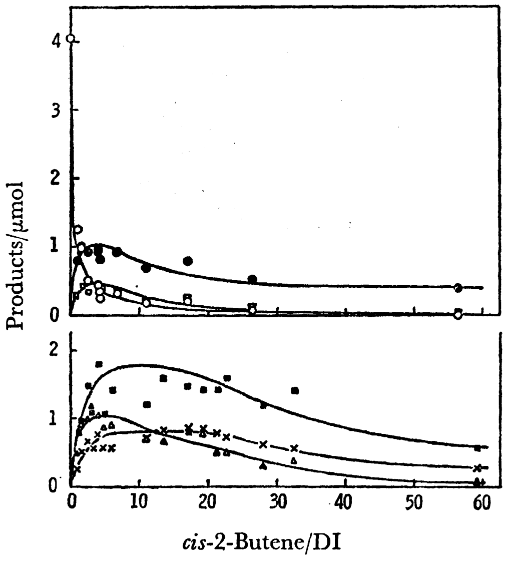

Fig. 1. The photolysis products as a function of the *cis*-2-butene/DI ratio. ○, D_2; ●, HD; □, CH_3D; ■, *n*-butane; △, propylene; ×, 1-butene.

Mass-spectrometric analysis showed that the methane formed in the present system consisted of CH_3D and CH_4. By estimating the contribution of the HI initially present in the DI gas, and that of the abstraction reaction of CH_3 from butene, to the formation of CH_4,$^{4)}$ it was concluded that, if pure DI was used, all of the methane produced must be CH_3D. When a similar correction was applied to the mass spectra of propylene and *n*-butane, it was found that they were $CH_3CH{=}CHD$ and $CH_3CHDCHDCH_3$ respectively. In the case of 1-butene, however, no unique conclusion could be obtained.

According to Back and Cvetanović, iodine atoms initiate the *cis-trans* isomerization of 2-butene, and also the isomerization to 1-butene, although the latter process is very slow.[5] In the present system, obviously, these reactions are overlapped with the reactions initiated by the D atoms. Therefore, we will not discuss the formation of 1-butene in the present system, although it is itself of much interest.

Discussion

Abstraction Reaction of Hot D Atoms. As Fig. 1 shows, the amounts of HD, CH_3D, and $CH_3CH{=}CHD$ increase with the increase in the ratio of *cis*-2-butene/DI up to about 3, where the total pressure is 40 Torr. At the pressures higher than that, the three products gradually decrease with the increase in pressure. The curve for HD levels off at about 0.4 μmol, while those for CH_3D and $CH_3CH{=}CHD$ approach zero. The curve for HD is very similar to that obtained in the DI–C_3H_6 system.[2] These results may be interpreted in terms of the following reaction scheme:

$$\mathrm{DI} + h\nu \longrightarrow \mathrm{D^*} + \mathrm{I} \qquad (1)$$

$$\mathrm{D^*} + \mathrm{DI} \longrightarrow \mathrm{D_2} + \mathrm{I} \qquad (2)$$

$$\mathrm{D^*} + \mathrm{I_2} \longrightarrow \mathrm{DI} + \mathrm{I} \qquad (3)$$

$$\mathrm{D^*} + \mathrm{C_4H_8} \left\{ \begin{array}{ll} \longrightarrow \mathrm{D} + \mathrm{C_4H_8} & (4) \\ \longrightarrow \mathrm{HD} + \mathrm{C_4H_7} & (5) \\ \longrightarrow \mathrm{C_4H_8D^*} & (6) \end{array} \right.$$

$$\mathrm{C_4H_8D^*} \left\{ \begin{array}{ll} \longrightarrow \mathrm{CH_3} + \mathrm{CH_3CH{=}CHD} & (7) \\ \longrightarrow \mathrm{H} + \mathrm{C_4H_7D} & (8) \\ \longrightarrow \mathrm{D} + \mathrm{C_4H_8} & (9) \end{array} \right.$$

$$\mathrm{C_4H_8D^*} + \mathrm{M} \longrightarrow \mathrm{C_4H_8D} + \mathrm{M} \qquad (10)$$

$$\mathrm{C_4H_8D} + \mathrm{DI} \longrightarrow \mathrm{C_4H_8D_2} + \mathrm{I} \qquad (11)$$

$$\mathrm{C_4H_8D} + \mathrm{I_2} \longrightarrow \mathrm{C_4H_8DI} + \mathrm{I} \qquad (12)$$

$$\mathrm{CH_3} + \mathrm{DI} \longrightarrow \mathrm{CH_3D} + \mathrm{I} \qquad (13)$$

$$\mathrm{CH_3} + \mathrm{I_2} \longrightarrow \mathrm{CH_3I} + \mathrm{I} \qquad (14)$$

$$\mathrm{CH_3} + \mathrm{C_4H_8} \longrightarrow \mathrm{C_5H_{11}} \qquad (15)$$

$$\mathrm{H(D)} + \mathrm{DI} \longrightarrow \mathrm{HD(D_2)} + \mathrm{I} \qquad (16)$$

$$\mathrm{H(D)} + \mathrm{I_2} \longrightarrow \mathrm{HI(DI)} + \mathrm{I} \qquad (17)$$

$$\mathrm{H(D)} + \mathrm{C_4H_8} \longrightarrow \mathrm{C_4H_9(C_4H_8D)} \qquad (18)$$

$$\mathrm{I} + \mathrm{I} + \mathrm{M} \longrightarrow \mathrm{I_2} + \mathrm{M} \qquad (19)$$

In the presence of a large amount of *cis*-2-butene, all of the thermalized atoms and radicals are captured by *cis*-2-butene or I_2 and do not contribute to the formation of HD and CH_3D. Therefore, the HD formation observed at the higher pressures must be due to Reaction (5). In the absence of *cis*-2-butene, the amount of D_2 produced was 4.02 μmol. Using this value and assuming $k_1/k_2=3$,[6] the ratio of $k_5/(k_4+k_5+k_6)$ may be estimated to be as follows: $0.4/4.02(1+3\times 1.1/10.3)=0.075$. This value, about 8%, is smaller than that previously obtained as the fraction of the abstraction reaction in the hot D atom reaction in the DI–C_3H_6 system (more than 10%). By comparing the curves of HD in both experiments, we feel that the figure of more than 10% previously obtained may be a little overestimated. However, the exact determination of these values is not feasible by the present technique.

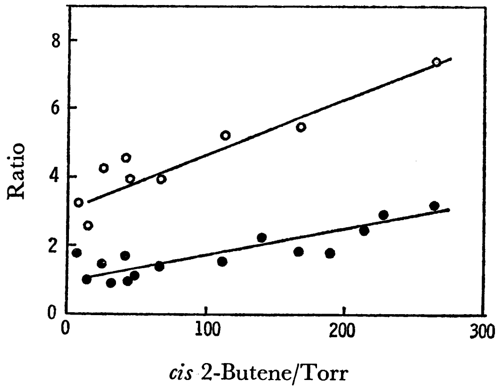

Fig. 2. The ratios of *n*-butane/methane (○) and *n*-butane/propylene (●) as a function of the *cis*-2-butene pressure.

Formation of CH_3D. Figure 2 shows the ratios of propylene/*n*-butane and methane/*n*-butane as a function of the pressure of *cis*-2-butene. On the appropriate assumption, the steady-state treatment of the reaction mechanism proposed above can predict these linear relationships.

In a previous paper, we concluded that the D* atoms produced in the photolysis of DI at 2288 Å did not give rise to the direct substitution reaction:

$$\mathrm{D^*} + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{CHD{=}CH_2} + \mathrm{H}$$

The mechanism of the methane formation discussed above may be taken as one of the evidences supporting this conclusion.

Reaction (7) is a unimolecular reaction which competes with Reactions (8) and (9). If the hot radical has a lifetime long enough for the distribution of its excess energy to the vibrational freedom of the radical, Reaction (7) may predominate over Reactions (8) and (9), because the excess energy retained in the radical is only 50 kcal/mol. However, the pressure-dependent curve of HD in the range of the C_4H_8/DI ratios, 0∼10, is similar to that of CH_3D, as is shown in Fig. 1. There are two possible explanations for this similarity. One is that the lifetime of the hot radical is not long enough for the distribution of the excess energy, upon which Reaction (8) depends. The other is the participation of the substitution reaction of hot D atoms, such as

$$\mathrm{D^*} + \mathrm{CH_3CH{=}CHCH_3} \longrightarrow \mathrm{CH_2DCH{=}CHCH_3} + \mathrm{H},$$

which may be possible, because the C–H bond, which is substituted, is aliphatic. Since we could not analyze the D content in *cis*-2-butene, though, no precise conclusion could be drawn.

General Discussion. The hot D atoms obtained in the present experiment are retained most at 2.4 eV.[2] According to the estimation of Wolfgang,[1] the characteristic hot atom reactions take place at more than 5 eV. The reactions reported here, therefore, are largely explainable by a small extension of the thermal reactions.

The decomposition of the *sec*-butyl radicals produced by the addition of hydrogen atoms to 2-butene has been extensively studied by Rabinovitch and his coworkers,[7] and chemical activation is a well-known method of obtaining the hot radicals. For the production of hydrogen atoms, they used an electric discharge under a low pressure of hydrogen. Their data were mainly obtained at pressures lower than 1 Torr. Therefore, the results obtained here cannot be compared directly with theirs. According to their data on the D+*cis*-2-butene system,[8] k_a is about $2.0\times10^7\ \mathrm{s}^{-1}$ at the pressure of 0.3 Torr. k_a is defined as follows:

$$k_a = \omega\frac{D}{S}$$

Here, ω is the collision frequency, while D and S are the fractions of the decomposition and of the stabilization of hot radicals. A rough estimation may be made in the present system as follows:

$$\frac{\text{methane}}{n\text{-butane}} \simeq \frac{D}{S} = k_a'/\omega$$

Using the data shown in Fig. 2, the value of k_a' could be calculated to be in the range of $10^8\ \mathrm{s}^{-1}$, which is a little larger than the k_a value reported for the thermal D atom reaction. This difference may be attributed to the difference in the initial energy of the D atoms.

References

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