The Reactions of Hot Deuterium Atoms with Ethylene

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The reactions of hot hydrogen atoms with hydrocarbons have been extensively investigated, using recoil tritium from the nuclear reaction.[1,2] The energy with which hydrogen atoms efficiently react with the substrate is not certain, however. Consequently, the photolysis of hydrogen halides and hydrogen sulfide has received renewed attention as the source of hot hydrogen atoms.[3-5]

We have recently studied the 2288 Å photolysis of DI–C_2H_4 mixtures. The excess energy of the D atoms produced ranges from 1.4 to 2.3 eV.[6,7] Since ethylene is a well-known scavenger for thermal hydrogen atoms, it may be one of the most suitable substrates for investigating the hot hydrogen atom-reactions. Nevertheless, very few measurements with this compound have been reported.

The deuterium iodide used was synthesized by heating a mixture of deuterium and iodine on platinized asbestos in a Pyrex tube at 400°C for two days. During the storage of DI gas in the bulb covered with Al-foil, the HI content gradually increased, probably because of the proton-exchange reaction between DI and water in glass or in grease. The initial content of HI was less than 5%; when the content reached over 15%, the DI gas was renewed. The amounts of the products were measured volumetrically with a Toepler pump, and their analyses were made by mass spectrometry.

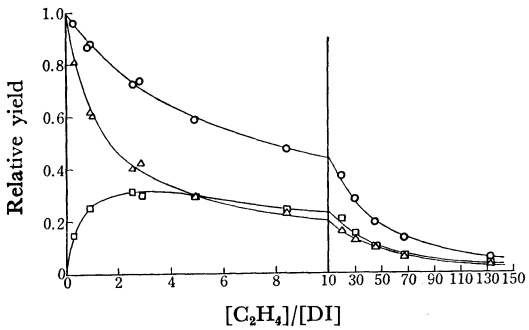

Fig. 1. The relative yields of total hydrogen (○), D_2 (△), and HD (□) as a function of the $[C_2H_4]/[DI]$ ratio. The yield of D_2 in the photolysis of pure DI was taken as unity. Initial DI pressure is 5 Torr and the irradiation time 6 min.

Figure 1 shows the relative yields of total hydrogen, D_2, and HD as a function of the $[C_2H_4]/[DI]$ ratio. The values are corrected for the HI contamination, the isotope effect being disregarded. Every run was sandwiched by the photolysis of pure DI so that the relative yield could be calculated accurately.

The HD formation may be explained in terms of such reactions of hot D atoms with ethylene as:

$$D^* + C_2H_4 \longrightarrow C_2H_3 + HD \quad (1)$$

and/or:

$$D^* + C_2H_4 \longrightarrow C_2H_3D + H \quad (2)$$

followed respectively by:

$$C_2H_3 + DI \longrightarrow C_2H_3D + I \quad (3)$$

and/or:

$$H + DI \longrightarrow HD + I \quad (4)$$

Mass-spectrometric analysis showed that the C_2 fraction in the product contained neither ethane nor acetylene, but C_2H_3D. Table 1 shows the $[C_2H_3D]/[HD]$ ratio as a function of the initial $[C_2H_4]/[DI]$ ratio, the values of which have already been corrected both for the HI contamination and for the C-13 natural abundance.

Table 1. The $[C_2H_3D]/[HD]$ ratio as a function of the initial $[C_2H_4]/[DI]$ ratio

The irradiation time is 6 min, the estimated conversion of DI being 25%.

$[C_2H_4]/[DI]$	0.27	0.83	2.51	8.35
$[C_2H_3D]/[HD]$	1.5	2.0	1.8	2.0

These results seem to substantiate the occurrence of the hot atom reactions described above. Moreover, the fact that the $[C_2H_3D]/[HD]$ ratio is more than unity suggests that Reaction (2) cannot be ignored in this system. If only Reaction (1) is responsible for the formation of HD, the $[C_2H_3D]/[HD]$ ratio should be less than unity, because a part of the C_2H_3 radicals formed react with the I_2 which is eventually formed in this system and produce no C_2H_3D. On the other hand, if Reaction (2) is more predominant than Reaction (1), the ratio should be more than unity, because a part of the H atoms produced in Reaction (2) react with I_2 and do not contribute to the formation of HD. I_2 molecules are an inevitable product in this system, and the rate constant of the $H+I_2 \rightarrow HI+I$ reaction is known to be more than ten times that of the $H+HI \rightarrow H_2+I$ reaction for the thermalized H atoms.[8]

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