The 2288 Å Photolysis of Hydrogen Iodide in the Presence of Ethylene and Propylene

Yasuhisa SANO and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received August 15, 1972)

The photolysis of hydrogen iodide at 2288 Å has been investigated in the presence of ethylene or propylene. The combinations studied were DI–C_2H_4, HI–C_2D_4, and DI–C_3H_6. In all combinations, the formation of a large amount of HD was observed; this may be attributed to the reaction of hot hydrogen atoms. The pressure dependence of the relative yields of HD and total hydrogen suggested that, of the two possible hot hydrogen atom reactions with ethylene, the abstraction reaction,

$$D^* + C_2H_4 \longrightarrow C_2H_3 + HD \quad (2)$$

does not occur, while the substitution reaction,

$$D^* + C_2H_4 \longrightarrow C_2H_3D + H \quad (3)$$

is the important process. In the case of propylene, however, the abstraction of H by D* is important for the formation of HD. The measured ratios of C_2H_3D/HD in the DI–C_2H_4 system and of C_2D_3H/HD in the HI–C_2D_4 system were consistent with the above conclusion. Reaction (3) is probably not a real substitution reaction, but a combination of the addition reaction of a hydrogen atom to ethylene and the rapid decomposition of the excited ethyl radical produced.

When hydrogen iodide is photolyzed at 2288 Å, hot hydrogen atoms are produced.[1,2] The excess translational energy amounts to 2.3 eV if the iodine atoms produced are in their ground state ($^2P_{3/2}$). According to the estimation of Compton and Martin,[2] about 20% of total iodine atoms are produced in the first excited state ($^2P_{1/2}$) in the 2288 Å photolysis of hydrogen iodide. In this case, the excess energy of hydrogen atoms is reduced to 1.4 eV.

In a previous communication,[3] we have suggested that the deuterium atoms produced in the photolysis of deuterium iodide at 2288 Å undergo the following reaction:

$$D^* + C_2H_4 \longrightarrow C_2H_3D + H$$

The present paper will report the details of this experiment, and also the results with different combinations, HI–C_2D_4 and DI–C_3H_6.

Experimental

Materials. The deuterium iodide was synthesized by heating a mixture of deuterium (Takachiho Chemical Co.) and iodine (Koso Chemical Co.) on platinized asbestos in a Pyrex tube at 400 °C for two days. The DI thus produced was distilled three times from a bath at 200 K to that at 77 K, with the rejection of the head and tail fractions. The DI gas thus synthesized was stored in a bulb covered with Al-foil. During the storage, the HI content gradually increased, probably because of a proton-exchange reaction between DI and water in glass or in grease. The HI content was estimated from the H_2 : HD : D_2 ratio obtained in the photolysis of DI. Since the extinction coefficient of HI at 2288 Å is a little larger than that of DI,[4] the HI content will be overestimated. The initial content of HI was less than 5%. When the content reached 15%, the reactant gas was renewed.

The hydrogen iodide was prepared by dropping hydriodic acid (Yanagishima Pharmaceutical Co.) on phosphorus pentoxide (Kishida Chemical Co.) cooled at 0 °C in a flow of nitrogen gas.

The C_2H_4, C_3H_6 (Takachiho Chemical Co.) and C_2D_4 (Merck Sharp & Dohme Co.) were used after bulb-to-bulb distillations. Mass spectrometric analysis showed that C_2D_4 contained 4% C_2D_3H.

Apparatus and Procedure. Home-made cadmium resonance lamps[5] were used for irradiation. When, of the two resonance lines, the 2288 Å line was cut off with the Toshiba UV-D 25 filter, the reaction products were very few. Therefore, all the measurements were carried out without a filter. The contribution of the 3261 Å resonance line to the reaction must be less than a few percent, because the extinction coefficient of hydrogen iodide at 2288 Å is about 200 $l \cdot mol^{-1} \cdot cm^{-1}$ and that at 3261 Å is a hundred times smaller.[6]

Before irradiation, all the faces of the quartz reaction vessel, 5 cm long and 5 cm in diameter, were heated with a torch under a vacuum to remove any deposit; however, the complete removal of iodine could not be achieved. All the experiments were done at room temperature. Immediately before and after the run with hydrocarbons, the photolysis of DI or HI without hydrocarbons was made in order to estimate the intensity of the light and in order to obtain the HI content when DI was used as a reactant. If the two measurements, before and after the run with hydrocarbons, did not agree within the limits of experimental error, this series of measurements was discarded.

The amounts of the products were measured volumetrically with a Toepler pump, and their analyses were made by mass spectrometry. Before the analysis of the H_2 : HD : D_2 ratio, it was determined that no significant isotope exchange was induced during the mass-spectrometric analysis. When the amount of C_2H_3D or C_2D_3H in ethylene was estimated, the correction for the ^{13}C natural abundance was applied to the data. Because of the presence of a large amount of C_2H_4 or C_2D_4, the estimated values of C_2H_3D

1) R. J. Carter, W. H. Hamill, and R. R. Williams, Jr., *J. Amer. Chem. Soc.*, **77**, 6457 (1955).
2) L. E. Compton and R. M. Martin, *J. Phys. Chem.*, **73**, 3474 (1969).
3) Y. Sano and S. Sato, This Bulletin, **44**, 3213 (1971).
4) J. R. Bates, J. O. Halford, and L. C. Anderson, *J. Chem. Phys.*, **3**, 415 (1935).
5) S. Tsunashima and S. Sato, This Bulletin, **41**, 284 (1968).
6) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999 (1964).

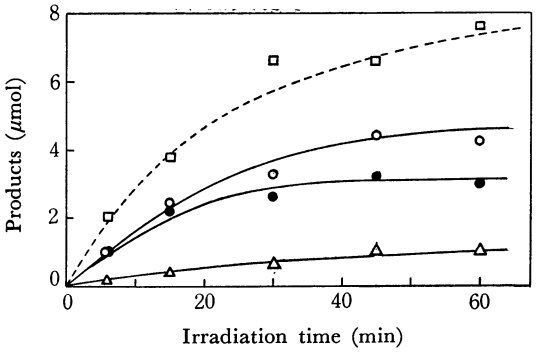

Fig. 1. The irradiation time dependence of the products in the 2288 Å photolysis of DI in the presence of C_2H_4.
□: C_2H_3D, ○: HD, ●: D_2, △: H_2

and C_2D_3H are not accurate, the error probably being ±50%.

Results

DI-C_2H_4. Figure 1 shows the time dependence of the products, D_2, HD, H_2, and C_2H_3D, from the photolysis of DI–C_2H_4 mixture. The DI gas used here contained 15% HI. The initial pressure of deuterium iodide was 5 Torr, and the initial $[C_2H_4]_i/[DI]_i$ ratio was 0.85. Since the contamination of HI could not be avoided, the following procedure was applied to the experimental results as correction. In the first place, the ratios of $x=[HD]_0/[D_2]_0$ and $y=[H_2]_0/[D_2]_0$ were calculated. Here, the suffix 0 denotes the absence of C_2H_4. Then the following correction was applied to the data:

$$[HD]_{corr} = [HD]_e - [D_2]_e x$$

$$[H_2]_{corr} = [H_2]_e - [D_2]_e y$$

Here, the suffix e denotes the presence of C_2H_4, while the suffix corr denotes the corrected values. The $[H_2]_{corr}$ values thus obtained were always very close to zero.

Figure 2 shows the relative yields of D_2+HD, D_2, and HD as a function of the initial ratio of C_2H_4 to DI. Here, the initial pressure of DI was kept at 5 Torr and the pressure of C_2H_4 was changed. The conversion of DI was less than 20%. The yield of D_2 in the photolysis of DI was taken as unity. The correction described above has already been applied. Table 1 shows the $[C_2H_3D]/[HD]$ ratio, which was

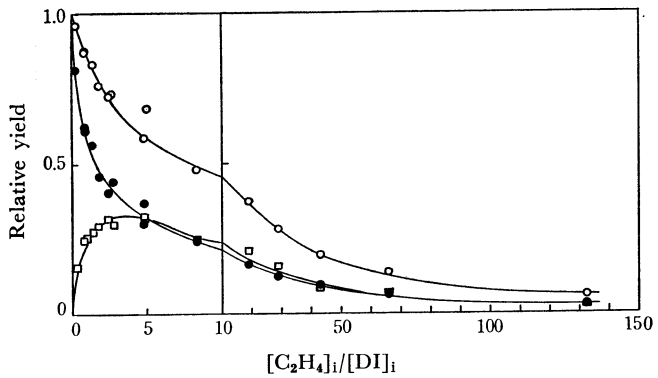

Fig. 2. The relative yields of D_2+HD (○), D_2 (●), and HD (□) as a function of the initial $[C_2H_4]_i/[DI]_i$ ratio.

Table 1. The $[C_2H_3D]/[HD]$ ratio as a function of the $[C_2H_4]_i/[DI]_i$ ratio. (The initial pressure of DI is 5 Torr. Irradiation time is 6 min.)

$[C_2H_4]_i/[DI]_i$	$[C_2H_3D]/[HD]$
0.27	1.5
0.84	1.5
1.40	2.4
1.88	1.5
2.51	1.8
8.35	2.0

obtained in the same series of data measurement as is shown in Fig. 2. At $[C_2H_4]_i/[DI]_i$ ratios higher than 10, the $[C_2H_3D]/[HD]$ ratios could not be measured because of a large amount of C_2H_4. In spite of the careful inspection of the mass spectrograms, no products other than C_2H_3D, such as acetylene or ethane, could be observed.

HI-C_2D_4. The relative yields of H_2+HD, H_2, and HD are shown in Fig. 3 as a function of the $[C_2D_4]/[HI]_i$ ratio. In this case, no correction except the contribution of 4% C_2D_3H in C_2D_4 to the observed yields was necessary. Table 2 shows the $[C_2D_3H]_i/[HD]_i$ ratio as a function of the $[C_2D_4]_i/[HI]_i$ ratio. Several measurements were made in the presence of the saturated vapor pressure of iodine, which was intentionally introduced in the system. Practically no difference between the data obtained in the presence and in the absence of iodine was observed. The

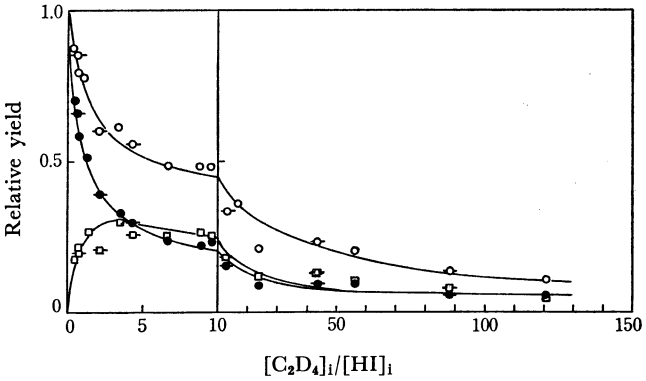

Fig. 3. The relative yields of H_2+HD (○), H_2 (●), and HD (□) as a function of the initial $[C_2D_4]_i/[HI]_i$ ratio. The bar means the presence of the iodine intentionally introduced.

Table 2. The $[C_2D_3H]/[HD]$ ratio as a function of the $[C_2D_4]_i/[HI]_i$ ratio. (The initial pressure of HI is 5 Torr. Iodine vapor was intentionally introduced.)

$[C_2D_4]_i/[HI]_i$	Irradiation time (min)	$[C_2D_3H]/[HD]$
0.41	6	0.7
0.74	6	1.3
1.24	6	0.9
3.39	6	1.0
0.71	16	0.8
2.09	16	2.0
4.27	16	1.9

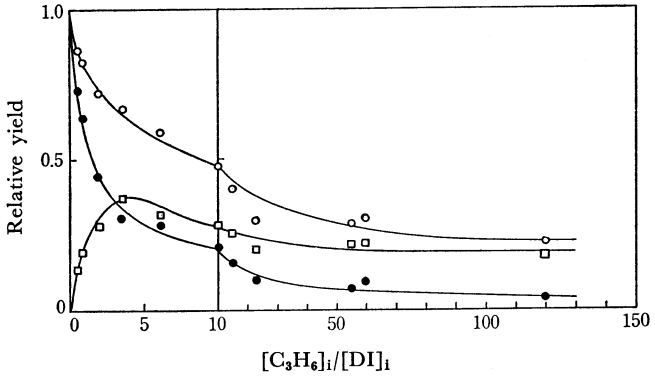

Fig. 4. The relative yields of D_2+HD (○), D_2 (●), and HD (□) as a function of the initial $[C_3H_6]_i/[DI]_i$ ratio.

$[C_2D_3H]/HD]$ ratios obtained in this series of experiments are also shown in Table 2.

DI-C_3H_6. Propylene was also used as a counterpart in the photolysis of DI. Figure 4 shows the relative yields of D_2+HD, D_2, and HD as a function of the $[C_3H_6]_i/[DI]_i$ ratio. A correction similar to that to the DI-C_2H_4 system has already been applied. Obviously the curves for D_2+HD, D_2, and HD are very similar to those obtained with C_2H_4; however, the [HD] values do not approach zero, but level off at about 0.2. The mass-spectrometric analysis for the formation of C_3H_5D could not be carried out because the attempt to separate propylene from deuterium iodide was not successful.

Discussion

It is well known that the reaction of thermal hydrogen atoms with ethylene or propylene leads almost exclusively to the formation of the ethyl or isopropyl radical. According to the estimation of Jennings and Cvetanović,[7] the k_a/k_b ratios are zero for ethylene and 0.045 for propylene.

$$H + RH \longrightarrow H_2 + R \qquad a$$

$$H + RH \longrightarrow RH_2 \qquad b$$

Woolley and Cvetanović reinvestigated these ratios and reported zero for ethylene and 0.082 for propylene. Therefore, the formation of a large amount of HD observed in the present experiment may be considered to be evidence for a hot hydrogen atom reaction. However, the reaction of the (a) type is not necessarily the only mechanism for the formation of HD. Another possible mechanism is the following substitution reaction:

$$D^* + RH \longrightarrow H + RD$$

followed by:

$$H + DI \longrightarrow HD + I$$

Such a substitution reaction has been observed with recoil tritium atoms from a nuclear reaction.[8] Which type of reaction is responsible for the formation of HD is one of the main concerns in this paper.

As Figs. 2 and 3 show, the formation of HD in the system containing ethylene approaches zero with the increase in the ratio of ethylene to hydrogen iodide. This result suggests that the hot hydrogen atom does not abstract a hydrogen atom from ethylene in the first collision. If it does, a certain fraction of HD should remain even at the higher $[C_2H_4]_i/[DI_i]$ ratios, because the $[DI]_i$ was kept at a constant value, 5 Torr. In the system containing propylene, on the other hand, the HD formation levels off at a constant value with the increase in propylene, as is shown in Fig. 4.

In order to discuss these reactions, the following reaction scheme was considered:

$$DI + h\nu \rightarrow D^* + I \qquad (0)$$

$$D^* + DI \rightarrow D_2 + I \qquad (1)$$

$$D^* + RH \rightarrow HD + R \qquad (2)$$

$$D^* + RH \rightarrow H + RD \qquad (3)$$

$$D^* + RH \rightarrow D + RH \qquad (4)$$

$$D^* + I_2 \rightarrow DI + I \qquad (5)$$

$$D + DI \rightarrow D_2 + I \qquad (6)$$

$$D + RH \rightarrow RHD \qquad (7)$$

$$D + RH \rightarrow HD + R \qquad (8)$$

$$D + I_2 \rightarrow DI + I \qquad (9)$$

$$H + DI \rightarrow HD + I \qquad (10)$$

$$H + RH \rightarrow RH_2 \qquad (11)$$

$$H + RH \rightarrow H_2 + R \qquad (12)$$

$$H + I_2 \rightarrow HI + I \qquad (13)$$

$$R + DI \rightarrow RD + I \qquad (14)$$

$$R + RH \rightarrow R_2H \qquad (15)$$

$$R + I_2 \rightarrow RI + I \qquad (16)$$

$$I + I + M \rightarrow I_2 + M \qquad (17)$$

For the discussion of the HI–C_2D_4 system, H and D in the scheme should be exchanged. In this reaction scheme, the moderation of D* atoms by DI and I_2 was not included, because the heavy molecules, such as DI and I_2, would not be effective moderators for hot hydrogen atoms. Table 3 summarizes the average fraction of energy lost per collision, assuming an elastic head-on collision. According to the estimation of Martin and Willard,[6] the average fractions of energy lost per collision in the systems of $H^*+C_2D_6$ and of $D^*+C_2H_6$ are, respectively, 0.19 and 0.51, values which are 1.5 and 2 times that of the energy lost per elastic head-on collision. Ob-

Table 3. Average fraction (f) of the energy lost per elastic head-on collision

Reactants	f
H^* + HI	0.03
D^* + DI	0.06
H^* + C_2D_4	0.12
D^* + C_2H_4	0.25

7) K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961); G. R. Woolley and R. J. Cvetanović, *ibid.*, **50**, 4705 (1969).

8) J. W. Root, W. Breckenridge, and F. S. Rowland, *ibid.*, **43**, 3694 (1965).

viously, even in the case of 2.3 eV D* in C_2H_4, several collisions are necessary for the complete thermalization. In the present treatment, however, it has been assumed that only one collision is effective enough to thermalize the hot hydrogen atom; otherwise, the kinetic treatment cannot easily be carried out.

When the conversion is not large, the steady-state-treatment on the reasonable assumptions that $k_3 \gg k_8$ and that $k_1[DI] \gg k_5[I_2]$ gives the following relationship: Here, ϕ denotes the relative yield of $[D_2]+[HD]$, and β stands for the following ratio:

$$\frac{1-\beta}{1-\phi} = 1 + \frac{k_2}{k_3+k_4} + \frac{k_1}{k_3+k_4}\frac{[DI]}{[RH]} \qquad (I)$$

$$\beta^{-1} = 1 + \frac{k_7[RH]}{k_6[DI]} + \frac{k_9[I_2]}{k_6[DI]}$$

$$= 1 + \frac{k_{11}[RH]}{k_{10}[DI]} + \frac{k_{13}[I_2]}{k_{10}[DI]} \qquad (II)$$

The equality between the second equation and the third in Eq. (II) is acceptable, because Reactions (6), (7), and (9) are the reactions of deuterium atoms DI, RH, and I_2 respectively, while Reactions (10), (11), and (13) are those of hydrogen atoms with DI, RH, and I_2 respectively.

Since Reactions (10), (11), and (13) are those of thermal hydrogen atoms, the specific rates are rather accurately known. According to the measurements of Penzhorn and Darwent,[9,10] the ratio of k's for the reactions of thermal hydrogen atoms with I_2 and HI is expressed by $4.96\exp(640/RT)$, and $k(H+C_2H_4)/k(H+HI)$ is equal to $0.30\exp(-845/RT)$. Cvetanović and Doyle reported $k(H+C_3H_6)/k(H+C_2H_4)=1.53$ at 20 °C.[11] For the present calculations, the following values were used: 0.0738 for k_7/k_6 of ethylene, 0.113 for k_7/k_6 of propylene, and 14.3 for k_9/k_6. As has been described in the results for the system of HI–C_2D_4, the intentionally-introduced iodine did not affect the formation of H_2 and HD. Judging from this result and from the difficulty in completely removing iodine in the reaction vessel, it may be said that all the reactions reported here take place in the presence of iodine vapor. Therefore, the following calculations were carried out on the assumption that the iodine pressure in the reaction vessel was 0.195 Torr, the saturated vapor pressure of iodine at 20 °C.[12]

Figure 5 shows the plots of the left-hand side of Eq. (I) as a function of the [Deuterium iodide]/[Olefin] ratio. From these linear relationships, the values listed in Table 4 were obtained. It may be noticed here that the value of k_2 is very small in the case of ethylene.

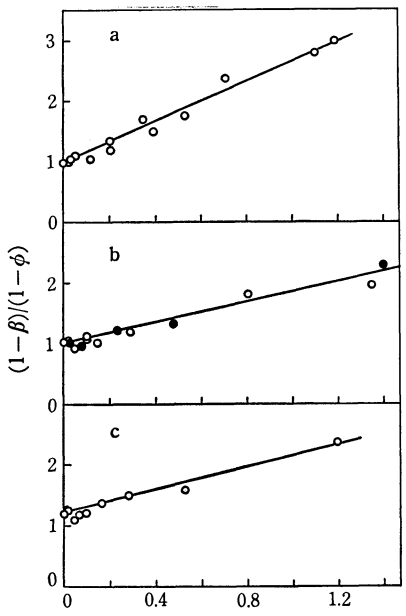

Fig. 5. The plots for Eq. (I).
a: $[DI]_i/[C_2H_4]_i$, b: $[HI]_i/[C_2D_4]_i$, c: $[DI]_i/[C_3H_6]_i$

TABLE 4. THE CALCULATED VALUES OF THE RATIOS OF k'S

System	$k_2/(k_3+k_4)$	$k_1/(k_3+k_4)$	
C_2H_4–DI	0.0	1.6	$k_1 \gg k_2$
C_2D_4–HI	0.0	0.85	
C_3H_6–DI	0.2	1.0	$k_1=5k_2$

The steady-state treatment based on the reaction scheme proposed above also gives this relation:

$$\frac{\phi_D}{\phi_{HD}} = \frac{\beta k_4}{k_2+\beta k_3} + \frac{k_1}{k_2+\beta k_3}\frac{[DI]_i}{[C_2H_4]_i} \qquad (III)$$

In the system of DI–C_2H_4, the value of k_2 may be taken to be zero; then, the plots of ϕ_{H_2}/ϕ_{HD} as a function of $[DI]_i/\beta[C_2H_4]_i$ should give a straight line. Similarly, in the HI–C_2D_4 system the ϕ_{H_2}/ϕ_{HD} ratio should be linearly dependent on the $[HI]_i/\beta[C_2D_4]_i$ ratio. The results are shown in Fig. 6. The slopes and the intercepts of the straight lines give $k_4/k_3 \sim 0.7$ and $k_1/k_3 \sim 1.0$ for both systems. However, these values should not be taken too seriously, because in them errors from various sources are accumulated. Therefore, the only thing we can say is that all the values of k_1, k_3, and k_4 are in the same order.

Consequently, we can conclude from the above two analyses that the k_2 is much smaller than the k_3 in the system with ethylene and that the k_2 is more than 20% of the k_3 in the system with propylene.

In the experiments on the DI–C_2H_4 and HI–C_2D_4 systems, we measured the amounts of C_2H_3D and C_2D_3H produced. The ratios of $[C_2H_3D]/[HD]$ and $[C_2D_3H]/[HD]$ are listed in Tables 1 and 2. Although the data are very scattered, they may be enough to show that the ratios are between 1.0 and 2.0.

Since we know that thermal hydrogen atoms are about 10 times more reactive to hydrogen iodide than

9) R. D. Penzhorn and B. deB. Darwent, *J. Phys. Chem.*, **72**, 1639 (1968).
10) R. D. Penzhorn and B. deB. Darwent, *J. Chem. Phys.*, **55**, 1508 (1971).
11) R. J. Cvetanović and L. C. Doyle, *ibid.*, **50**, 4705 (1969).
12) L. J. Gillespie and L. H. D. Fraser, *J. Amer. Chem. Soc.*, **58**, 2260 (1936).

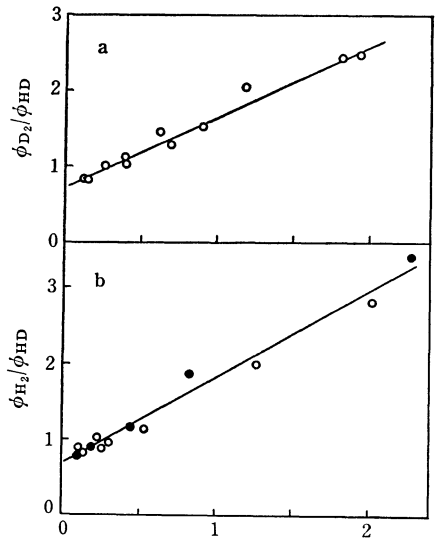

Fig. 6. The plots for Eq. (III).
a: $[DI]_i/\beta[C_2H_4]_i$, b: $[HI]_i/\beta[C_2D_4]_i$

to olefins, and since the C_2D_3H and C_2H_3D values were measured in the Olefin/Hydrogen Iodide ratio range of 0.4~8, we can derive the following relationship by using the steady-state treatment:

$$\frac{[RD]}{[HD]} = \frac{k_2+(1+\gamma)k_3}{k_3+(1+\gamma)k_2} \qquad \text{(IV)}$$

Here, γ stands for the following ratio:

$$\gamma = \frac{k_{13}[I_2]}{k_{10}[DI]} = \frac{k_{16}[I_2]}{k_{14}[DI]} \qquad \text{(V)}$$

The equality between the second term and the third in Eq. (V) may be admitted for the same reason as in the case of Eq. (II). At the temperature of 20 °C, the k_{13}/k_{10} ratio is equal to 14.3, as has already been stated. Therefore, the value of γ for the present experiment is calculated to be $0.6(=14.4\times0.195/5.0)$. In the above discussion, the inequality $k_2 \ll k_3$ has been derived in the DI–C_2H_4 and HI–C_2D_4 systems. The substitution of this relation into Eq. (IV) leads to the conclusion that the [RD]/[HD] ratio should be 1.6. This value is not inconsistent with the observed values.

In the discussion of the reactions of tritium atoms from a nuclear reaction with saturated hydrocarbons, Wolfgang indicated that the threshold energy of the substitution reaction is higher than that of the abstraction reaction.[13] If this rule is applicable to ethylene, the present conclusion, $k_2 \ll k_3$, is obviously inconsistent with the statement of Wolfgang. However, according to the paper presented by Turner and Cvetanović,[14] when D atoms produced by the mercury-photosensitized decomposition of n-C_4D_{10} add to C_2H_4, the isotopic exchange occurs, but it does not occur when H atoms add to C_2D_4. Comparing these results with ours, we believe that the substitution reaction observed in the present experiment occurs through the rapid decomposition of excited ethyl radicals produced, the internal energy of which is much higher than that of the ethyl radicals discussed by Turner and Cvetanović.

If the Kassel equation, $k=(1-\varepsilon_0/\varepsilon)^{s-1}$, is applicable to the unimolecular decomposition of ethyl radicals, the lifetime may be calculated to be in the order of 10^{-11} s by using the following values: $A=10^{13.6}$, $\varepsilon_0=40.7$ kcal mol^{-1},[15] $\varepsilon=40.7+50$, and $s=8$. This lifetime is obviously too short to be affected by the pressure used in the present experiment.

13) R. Wolfgang, "Progress in Reaction Kinetics," vol. 3, edited by G. Porter, Pergamon Press, (1965) p. 97.
14) A. H. Turner and R. J. Cvetanović, *Can. J. Chem.*, **37**, 1075 (1959).
15) H. E. O'Neal and S. W. Benson, "Kinetic Data on Gas Phase Unimolecular Reactions" NSRDS-NBS 21, U.S. Department of Commerce, N.B.S. (1970).