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A Shock Tube Study of the Decomposition Mechanism of Chloroform in the Presence of Deuterium or Methane

Takayuki YANO

Institute of Space and Aeronautical Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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Chloroform was pyrolyzed in the absence and in the presence of one of three additives—D_2, CH_4, and CD_4, over the temperature range of 1000—1200 K in a single-pulse shock tube. The main products of the decomposition of chloroform by itself were tetrachloroethylene and hydrogen chloride. On the other hand, tetrachloroethylene, trichloroethylene, dichloromethane, and hydrogen chloride were the major products in the presence of D_2, while in the chloroform–methane systems they were tetrachloroethylene, trichloroethylene, 1,1-dichloroethylene, vinyl chloride, ethane, and hydrogen chloride. From the deuterium distribution of the products, as determined by mass spectrometry, it is found that the hydrogen atoms of trichloroethylene and 1,1-dichloroethylene mainly came from chloroform and methane respectively, while the hydrogen atoms of vinyl chloride came from both chloroform and methane. The change in the product distribution resulting from the addition of deuterium or methane and the hydrogen isotopic distribution suggest that the mechanism is composed of Cl atom elimination in the initiation step and successive reactions involving "hot" molecule reactions. The hydrogen isotopic distribution of vinyl chloride may indicate that the three-centered hydrogen elimination ($\alpha\alpha$) process competes with the four-centered ($\alpha\beta$) process in the decomposition of "hot" 1,1-dichloroethane.

The decomposition of chloroform has been investigated by several authors. Among them, the studies of Semeluk and Bernstein[1)] and Shilov and Sabirova[2)] have been detailed. However, they came to different conclusions about the initiation process.

Semeluk and Bernstein[1)] investigated the decomposition of chloroform at about 800 K by the flow method; they found that hydrogen chloride and tetrachloroethylene (C_2Cl_4) were the main products and that the decomposition rate was first-order with respect to chloroform. They proposed the radical chain mechanism to explain the main product distribution and the kinetics;

$$CHCl_3 \longrightarrow CHCl_2\cdot + Cl\cdot, \tag{1}$$

$$Cl\cdot + CHCl_3 \longrightarrow CCl_3\cdot + HCl, \tag{2}$$

$$CCl_3\cdot \longrightarrow CCl_2{:} + Cl\cdot, \tag{3}$$

$$CCl_3\cdot + Cl\cdot \longrightarrow CCl_4, \tag{4}$$

$$CCl_2{:} + CHCl_3 \longrightarrow C_2Cl_4 + HCl. \tag{5}$$

On the other hand, Shilov and Sabirova[2)] studied the decomposition in a toluene carrier and found no bibenzyl. From their results, they proposed another mechanism;

$$CHCl_3 \longrightarrow CCl_2{:} + HCl, \tag{6}$$

$$CCl_2{:} + CHCl_3 \longrightarrow C_2Cl_4 + HCl. \tag{5}$$

It is desirable to investigate further the initiation step of the chloroform decomposition by the shock-tube technique, which enables us to neglect the surface reaction. Although the two mechanisms mentioned above produce the same main products and give similar kinetics of the first order, they produce different radicals in the initiation step. This provides a possible way to check both mechanisms. In order to detect the radicals formed in the initiation step, we pyrolyze chloroform in the presence of a relatively large amount of methane or hydrogen, whose decomposition itself can be neglected at the reaction temperatures. We found the change in the product distribution to result from the interaction between the radicals and the added gas molecule. Further, by the use of deuterated chloroform or deuterated additives, we also found the hydrogen isotopic distribution to be dependent upon the characteristics of the interaction.

Experimental

Apparatus. The decomposition was studied in a 4-cm-i.d. single-pulse shock tube. The design and operation of the shock tube were fully described previously.[3)]

Materials and Procedure. Chloroform of a research grade was purified as follows. In order to purge the trace of ethanol involved as a stabilizer, we first shook unpurified chloroform with concd H_2SO_4 in a separatory funnel, washed it with water, dehydrated it, and distilled it. Finally, we distilled chloroform three times under a vacuum. Deuterated chloroform obtained from E. Merck Co. was also distilled three times under a vacuum. Methane (99.5% purity) and deuterium of a research grade (99.5 D atom %) and argon of an ultra-high purity (99.999% purity) were used without further purification. A considerable amount of oxygen was present in the methane-d_4 (99.5 D atom %) of the Matheson Co.; it was removed by passing it through a reduced copper column.[4)] Experiments were carried out with the gas mixtures listed in Table 1.

TABLE 1. THE REACTANT MIXTURES AND THEIR COMPOSITIONS

Series No.	Components	Composition in mol%	
I	$CHCl_3/Ar$	1.5/98.5	
II	$CHCl_3/D_2/Ar$	1.5/4.8/93.7	
IIIa	$CHCl_3/CH_4/Ar$	2.4/4.6/93.0,	1.1/4.4/94.5
IIIb	$CHCl_3/CD_4/Ar$	1.8/3.7/94.5,	2.0/4.0/94.0
IIIc	$CDCl_3/CH_4/Ar$	1.0/7.8/91.2,	1.0/3.1/95.9
		1.9/5.8/92.3,	1.0/2.2/96.8

The hydrocarbons and chlorinated hydrocarbons were separated and analyzed on a Yanaco G-80 gas chromatograph equipped with a temperature programer. The gas sample was separated on a 2-m-long Porapak Q column, with He as the carrier gas; the separated components were detected by means of thermal-conductivity and flame-ionization detectors. As occasion demanded, we determined each eluted component by mass spectrometry in order to confirm the identification of each peak of the gas chromatography.

After the separation of the product gas mixture into components on a gas chromatograph, we analyzed the separated elutant by mass spectrometry in order to determine the hydrogen isotopic distribution. For the simplification of the mass spectrum, a low ionization voltage was employed. At an ionization voltage of about 10 eV, only the parent peak remained except for chloroform. In the case of chloroform, $CHCl_3$, the peak intensity of $CHCl_2^+$ was much stronger than that of $CHCl_3^+$, even at a low ionization voltage.

Results

The dwell time was practically constant (1 ms), and the total density behind the reflected shock waves was about $(2.4—3.9)\times10^{-5}$ mol/cm^3. The reaction temperature range was about 1000—1200 K. It was true in all the series that chlorinated ethylene and hydrogen chloride were the main products and that the chlorinated ethane was not present or, occasionally, present in a very small amount.[5] When one of the reactants was deuterated, the hydrogen isotopic isomers of chloroform were analyzed by mass spectrometry after the shock heating. It was thus confirmed that the isomer of chloroform converted by H/D exchange reaction was negligibly small. The experimental results for each series are described below.

Series I. Tetrachloroethylene and hydrogen chloride were produced predominantly. The hydrogen chloride was not quantitatively analyzed, since an exact determination of the yield is difficult because of the surface reactions. As the minor products, four species were found; trichloroethylene, dichloromethane, 1,1,2,2-tetrachloroethane, and an unidentified species. The characteristics of the product distribution were consistent with those reported of Semeluk and Bernstein.[1] Table 2 shows the yields of C_2Cl_4 and C_2HCl_3, together with the conversion of chloroform.

Series II. When deuterium was added, much more species were produced than those obtained from the decomposition of chloroform alone. Fifteen species involving unidentified peaks were detected. Trichloroethylene, which has been a minor product in Series I, here appeared as the main product. Tetrachloroethylene, dichloromethane, 1,1-dichloroethylene, vinyl chloride, and chloroacetylene were identified, while as trace species methane, ethylene, ethyl chloride, and 1,1,-2,2-tetrachloroethane were detected. The yields of the principal products are plotted against the chloroform conversion in Fig. 1.

Table 2. The concentrations of C_2Cl_4 and C_2HCl_3 in the product gas mixture and the conversion of chloroform

T/K	C_2Cl_4a)	C_2HCl_3a)	Chloroform conversionb)
975	135	13	c)
1005	320	26	c)
1033	310	21	c)
1058	770	44	18
1073	2300	48	40
1090	1690	77	39
1093	1680	75	39
1103	2370	116	51
1105	1770	84	43
1155	3350	33	80

a) The concentration is expressed in ppm. b) The conversion is expressed in %. c) The values in this column were obtained from the analysis of chloroform. The value denoted by c is slightly negative due to the analytical error.

As is shown in Fig. 1, trichloroethylene, C_2Cl_4, and dichloromethane increase linearly with the increase in the conversion at relatively low conversions, but they show their maximum at higher conversions. On the other hand, 1,1-dichloroethylene, vinyl chloride, and chloroacetylene were hardly detected at all at low conversions; they increased remarkably at high conversions.

The deuterium content of trichloroethylene is shown in Table 3. It should be noted that the yield of C_2HCl_3 is much greater than that of C_2DCl_3 over a wide conversion range.

Series III. Many species (13 species) were observed, as in the case of Series II. The principal products of the Series IIIa were 1,1-$C_2H_2Cl_2$, C_2H_3Cl, C_2H_6, C_2H_4, C_2HCl_3, and C_2Cl_4. Their yields, except for that of C_2Cl_4, are plotted against the chloroform conversion in Fig. 2 (C_2Cl_4 was not determined by gas

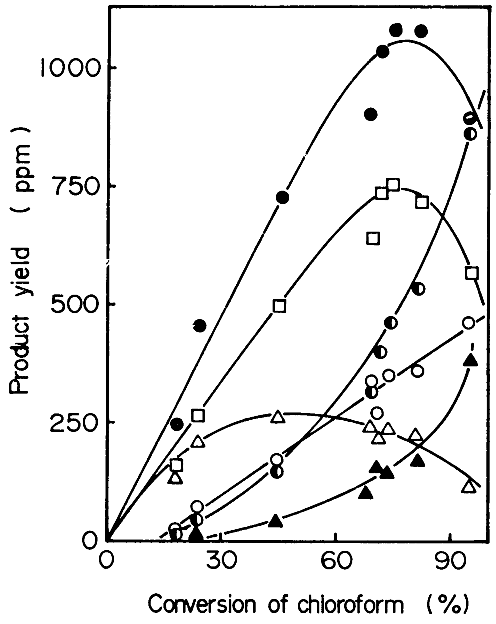

Fig. 1. Plots of product yield for series II, *vs.* chloroform conversion.
●: Trichloroethylene, □: C_2Cl_4, △: dichloromethane, ◐: 1,1-dichloroethylene, ▲: chloroacetylene, ○: vinyl chloride.

Table 3. Hydrogen isotopic distribution of trichloroethylene for series II

C_2HCl_3a)	C_2DCl_3a)	Chloroform conversiona)
91.8	8.2	23.0
87.8	12.2	43.6
78.0	22.0	67.7
72.2	27.8	72.6

a) These values are expressed in percentages.

chromatography, but the mass spectra showed the yield of C_2Cl_4 was comparable with that of C_2HCl_3). The product distributions of Series IIIb and IIIc were similar to that of Series IIIa.

The main hydrogen isotopic isomers of each product for Series IIIb and IIIc are shown in Table 4. When the conversion of chloroform is smaller than 50%, 1,1-dichloroethylene and trichloroethylene almost always consist of only one hydrogen isotopic isomer; the other isomers form less than one tenth of the main isomer. Vinyl chloride consists of two hydrogen isotopic isomers of comparable amounts.

In Table 4, if we replace the H and D atoms of Series IIIc by D and H atoms respectively, we obtain the distributions of the isotopic isomers of Series IIIb. The hydrogen of trichloroethylene came mainly from the reactant chloroform. On the contrary, the hydrogens of 1,1-dichloroethylene came from the reactant methane. The hydrogens of vinyl chloride, like 1,1-dichloroethylene, were supplied mainly by the methane, but partly by the chloroform.

Figure 3 shows the hydrogen isotopic distribution of vinyl chloride, which is dependent upon the temperature for Series IIIb and IIIc. The ratios of $[CHCl{=}CD_2]/[CDCl{=}CD_2]$ and $[CDCl{=}CH_2]/[CHCl{=}CH_2]$ for Series IIIb and IIIc respectively are plotted against the temperature. In the following discussion, it will be shown that they are equal to the ratio of the rate of the $\alpha\beta$ process to that of the $\alpha\alpha$ process in the decomposition of "hot" 1,1-dichloroethane. The $R_{\alpha\beta}/R_{\alpha\alpha}$ ratio decreases with an increase in both the temperature and the [methane]/[chloroform] ratio. There is no detectable isotope effect in the IIIb and IIIc series.

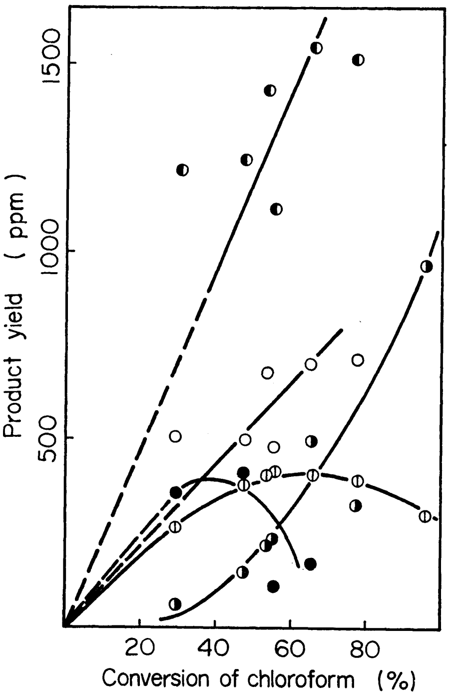

Fig. 2. Plots of product yield for series IIIa (1.1/4.4/94.5) *vs.* chloroform conversion.
◐: 1,1-Dichloroethylene, ○: vinyl chloride, ●: trichloroethylene, ⦶: ethane, ◑: ethylene.

TABLE 4. MAIN HYDROGEN ISOTOPIC ISOMERS OF CHLORINATED ETHYLENE FOR SERIES III

Species	Series IIIb	Series IIIc
Dichloroethylene	$C_2D_2Cl_2$	$C_2H_2Cl_2$
Vinyl chloride	C_2D_3Cl, C_2HD_2Cl	C_2H_3Cl, C_2H_2DCl
Trichloroethylene	a)	C_2DCl_3

a) This was not determined by mass spectrometry, but it may be C_2HCl_3 in view of the results of Series II and IIIc.

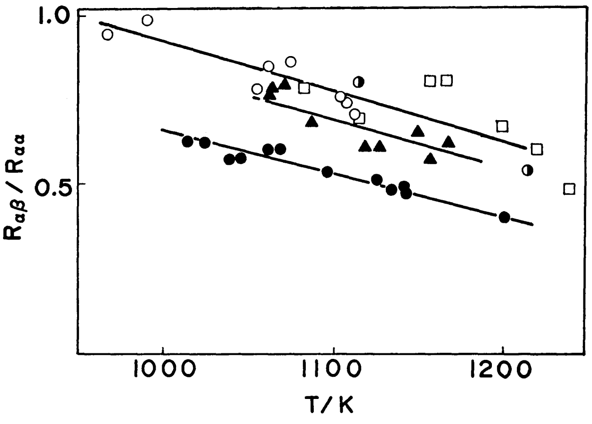

Fig. 3. Dependence of $R_{\alpha\beta}/R_{\alpha\alpha}$ on temperature and concentration ratio of $r=$[methane]/[chloroform] for series IIIb and IIIc. The ratio of $R_{\alpha\beta}/R_{\alpha\alpha}$ is equal to $[CHCl{=}CD_2]/[CDCl{=}CD_2]$ and $[CDCl{=}CH_2]/[CHCl{=}CH_2]$ for IIIb and IIIc, respectively.
□: $r=2.0$ (IIIb), ●: $r=7.8$ (IIIc), ▲: $r=3.1$ (IIIc), ○: $r=3.0$ (IIIc), ◑: $r=2.2$ (IIIc).

Discussion

The product distribution was changed drastically by the addition of methane or hydrogen. One of the characteristic changes is the decrease in C_2Cl_4; another is the increase in trichloroethylene.

In the case of D_2 addition, trichloroethylene, C_2Cl_4, and dichloromethane are supposed to be the primary products, because, in Fig. 1, their yields are linear to the conversion[6] at a low conversion. In the case of methane addition, ethane, vinyl chloride, 1,1-dichloroethylene, trichloroethylene, and C_2Cl_4 are probably the primary products, while ethylene is a secondary product, as may be seen from Fig. 2, although their plots are somewhat scattered.

The change in the product distribution can be readily explained by the Cl atom elimination, proposed by Semeluk and Bernstein,[1] from the chloroform molecule in the initiation step. In the case of D_2 addition, the Cl atom formed by Step 1 may abstract the D atom from the D_2 present in a large amount; then DCl and the D atom are produced;

$$Cl\cdot + D_2 \longrightarrow DCl + D\cdot\ . \qquad (7)$$

The D atom produced in Reaction 7 then further reacts with chloroform;

$$D\cdot + CHCl_3 \longrightarrow CHCl_2\cdot + DCl\ . \qquad (8)$$

Since there is a competitive relation between Reactions

7 and 2, Reaction 7 retards the radical-chain reaction to yield C_2Cl_4. On the other hand, because of the participation of Reaction 8, the formation rate of the $CHCl_2$ radical is increased. The "hot" molecule of 1,1,2,2-tetrachloroethane may be produced *via* the combination reaction of the $CHCl_2$ radical;

$$2CHCl_2\cdot \longrightarrow CHCl_2CHCl_2^* . \qquad (9)$$

The "hot" molecule is stabilized by collisions or decomposes to an ethylene-type molecule and hydrogen chloride *via* a unimolecular reaction;

$$CHCl_2CHCl_2^* \xrightarrow{+M} CHCl_2CHCl_2, \qquad (10)$$

$$\longrightarrow C_2HCl_3 + HCl. \qquad (11)$$

The fact that hardly no 1,1,2,2-tetrachloroethane is found may show that the "hot" molecule prefers the decomposition to the stabilization under our experimental conditions. Dichloromethane as a primary product may be formed *via* a hydrogen-abstraction reaction of the $CHCl_2$ radical;

$$CHCl_2\cdot + D_2 \longrightarrow CHDCl_2 + D\cdot. \qquad (12)$$

The production of C_2Cl_4 can be explained by the partly surviving chain reaction proposed by Semeluk and Bernstein.[1] It is apparent that the trichloroethylene produced through Reactions 9 and 11 has the same hydrogen isomer as the reactant chloroform.

On the other hand, the assumption by Shilov and Sabirova[2] that the CCl_2 radical is formed in the initiation step is not reasonable. In explaining the formation of trichloroethylene, the following plausible reactions are assumed on the basis of analogy with the CH_2 radical;

$$CCl_2{:} + D_2 \longrightarrow CDCl_2\cdot + D\cdot, \qquad (13)$$

$$D\cdot + CHCl_3 \longrightarrow CHCl_2\cdot + DCl . \qquad (8)$$

The decrease in the formation rate of C_2Cl_4 can be explained by the competition between Reactions 5 and 13. However, the yields of C_2HCl_3 and C_2DCl_3 which are produced from "hot" tetrachloroethanes would then be equal, since the formation rates of the $CHCl_2$ and $CDCl_2$ radicals are supposed to be equal. This expectation is not consistent with the experimental result; that is ,the formation of the CCl_2 radical in the primary step is doubtful. The increase in the composition of C_2DCl_3 with the increase in the conversion (Table 3) may be the result of some secondary reactions.[7]

In the case of the methane addition, in the IIIc series for example, the Cl atom elimination reaction also agrees with the experimental results. The following reactions may give C_1 radicals;

$$CDCl_3 \longrightarrow CDCl_2\cdot + Cl\cdot, \qquad (1)$$

$$Cl\cdot + CH_4 \longrightarrow CH_3\cdot + HCl , \qquad (14)$$

$$Cl\cdot + CDCl_3 \longrightarrow CCl_3\cdot + DCl. \qquad (2)$$

The "hot" ethane-type molecules are formed *via* the association of these C_1 radicals. These "hot" chlorinated ethanes decompose to ethylene-type molecules and hydrogen chloride. Ethane and C_2Cl_6 are only be stabilized by collisions;

$$2CDCl_2\cdot \longrightarrow CDCl_2CDCl_2^* \longrightarrow C_2DCl_3 + DCl, \qquad (11)$$

$$CDCl_2\cdot + CH_3\cdot \longrightarrow CDCl_2CH_3^* ,$$

$$\xrightarrow{\alpha\beta} CDCl{=}CH_2 + HCl , \qquad (15)$$

$$\xrightarrow{\alpha\alpha} CHCl{=}CH_2 + DCl , \qquad (16)$$

$$CDCl_2\cdot + CCl_3\cdot \longrightarrow$$

$$CDCl_2CCl_3^* \longrightarrow C_2Cl_4 + DCl , \qquad (17)$$

$$CH_3\cdot + CCl_3\cdot \longrightarrow$$

$$CH_3CCl_3^* \longrightarrow CH_2{=}CCl_2 + HCl , \qquad (18)$$

$$2CH_3\cdot \longrightarrow C_2H_6^* \xrightarrow{+M} C_2H_6 , \qquad (19)$$

$$2CCl_3\cdot \longrightarrow C_2Cl_6^* \xrightarrow{+M} C_2Cl_6 , \qquad (20)$$

All the products formed by Reactions 11 and 15—20 except C_2Cl_6 were identified as the primary products. The partly surviving chain mechanism as well as Reaction 17 may be responsible for the formation of C_2Cl_4, as in the case of D_2 addition.

The hydrogen isotopic distributions of trichloroethylene and 1,1-dichloroethylene through Reactions 11 and 18 are in good agreement with the experimental results. The assumption that the "hot" $CDCl_2CH_3$ molecule decomposes not only through the $\alpha\beta$ process but also through the $\alpha\alpha$ process can well explain the isotope distribution of vinyl chloride. It is well known that the haloethane eliminates hydrogen chloride *via* the $\alpha\beta$ process. Recently, however, Perona *et al.*[8] found the $\alpha\alpha$ process in the chemical activation study of the "hot" CHF_2CD_3, and its occurrence has lately been confirmed by Kim *et al.*[9] Moreover, Perona *et al.*[8] suggested that the $\alpha\alpha$ process was competitive with the $\alpha\beta$ process only when two halogen atoms are attached to the same carbon atom. It was also found from the studies of "hot" 1,1,2-trichloroethane-1-d_1[10] that the $\alpha\alpha$ process competed with the $\alpha\beta$ process. Therefore, the fact that the vinyl chloride consists of two hydrogen isotopic isomers may be evidence in support of the proposal by Perona *et al.*[8] Figure 3 indicates that the rate ratio of $R_{\alpha\beta}/R_{\alpha\alpha}$ decreases with the increase in the temperature; behavior like this has already been described by Perona *et al.*[8] and Kim *et al.*[9] This temperature dependence can be qualitatively explained by the RRK theory.[8,11] The $R_{\alpha\beta}/R_{\alpha\alpha}$ ratio is expressed by the following equation;

$$R_{\alpha\beta}/R_{\alpha\alpha} = \mathrm{A}_{\alpha\beta}(1-E^*_{\alpha\beta}/E)^{n-1}\{\mathrm{A}_{\alpha\alpha}(1-E^*_{\alpha\alpha}/E)^{n-1}\}^{-1}.$$

The number of effective oscillators, n, is assumed to be the same for both eliminations, and a value of $n=12$ has been adopted.[11] The internal energy, E, was taken to vary between 85.4 kcal/mol at 298 K and 109.6 kcal/mol[12] at 1200 K. The temperature dependence is ascertained by the choice of $E^*{}_{\alpha\beta}=52$ kcal/mol[13] and $E^*{}_{\alpha\alpha}=62$ kcal/mol. The difference in the critical energies ($E^*{}_{\alpha\alpha}-E^*{}_{\alpha\beta}$) is similar to that obtained by Perona *et al.*,[8] but is somewhat larger than that for "hot" 1,1,2-trichloroethane-1-d_1.[10] A more exact study will be necessary for a quantitative discussion.

In conclusion, in the case of methane addition, the product distribution and hydrogen isotopic distributions support the Cl atom elimination in the initiation step. On the contrary, the assumption that the CCl_2 radical is formed in the initiation step does not agree with the experimental results. If the following reactions were possible;

$$\mathrm{CCl_2{:}} + \mathrm{CH_4} \longrightarrow \mathrm{CHCl_2\cdot} + \mathrm{CH_3\cdot}, \qquad (21)$$

$$\mathrm{CCl_2{:}} + \mathrm{CDCl_3} \longrightarrow \mathrm{CDCl_2\cdot} + \mathrm{CCl_3\cdot}, \qquad (22)$$

the formation rate of C_2HCl_3 would be larger than that of C_2DCl_3, because Reaction 21 must be predominant over the Reaction 22 in the presence of excess methane. Vinyl chloride would be produced by the following reactions;

$$\mathrm{CHCl_2\cdot} + \mathrm{CH_3\cdot} \longrightarrow$$
$$\mathrm{CHCl_2CH_3}^* \longrightarrow \mathrm{CHCl{=}CH_2} + \mathrm{HCl}, \qquad (15')$$

$$\mathrm{CDCl_2\cdot} + \mathrm{CH_3\cdot} \longrightarrow$$
$$\mathrm{CDCl_2CH_3}^* \xrightarrow{\alpha\beta} \mathrm{CDCl{=}CH_2} + \mathrm{HCl}, \qquad (15)$$
$$\xrightarrow{\alpha\alpha} \mathrm{CHCl{=}CH_2} + \mathrm{DCl}. \qquad (16)$$

Reaction 15′ might be predominant over the others, and the yield of $CDCl{=}CH_2$ would be considerably small. These expectations are actually not in agreement with the experimental results. Further, the possibility of the insertion reaction of CCl_2 into C–H or a C–Cl bond and the successive elimination of hydrogen chloride may be considered. However, these reactions can not satisfactorily explain the variety of the products and the hydrogen isotopic distributions.

The reaction scheme based on the Cl atom elimination in the initiation step can well account for the variety of the products and their isotopic distributions. The scheme can not, however, explain the relative yields of the products without any modification. For the case of methane addition, 1,1-dichloroethylene was the main product, as is shown in Fig. 2. This can not be derived from the scheme. Under the experimental conditions, the formation rates of the C_1 radicals of $CDCl_2$, CH_3, and CCl_3 decrease in that order.[14] Therefore, the [vinyl chloride] > [1,1-dichloroethylene] relation might be expected. Perhaps this apparent contradiction can be solved by the assumption that there is another path to produced 1,1-dichloroethylene in addition to Reaction 18.

In the study of the chemical activation of CHF_2CD_3, Perona *et al.*[8] found the yield of $CF_2{=}CD_2$ to be about 1/2—1/10 of that of vinyl fluoride. They supposed a third unimolecular reaction path of "hot" CHF_2CD_3;

$$\mathrm{CHF_2CD_3}^* \longrightarrow \mathrm{CF_2{=}CD_2} + \mathrm{HD}. \qquad (23)$$

Kim *et al.*[9] also found $CF_2{=}CD_2$ in a similar reaction system and confirmed the unimolecular pressure dependence of the yield. Although they did not agree with the third unimolecular path because of its unusual nature, they could not find out any evidence denying it. Perona *et al.*[8] thought that Process 23 had a larger critical energy than those of the $\alpha\beta$ and $\alpha\alpha$ processes. The importance of the third path may, then, become greater at higher temperatures. The following reaction is assumed by analogy with Reaction 23;

$$\mathrm{CDCl_2CH_3}^* \longrightarrow \mathrm{CCl_2{=}CH_2} + \mathrm{HD}. \qquad (24)$$

Since Reaction 24 competes with the $\alpha\beta$ and the $\alpha\alpha$ processes, the formation rate of vinyl chloride decreases and that of 1,1-dichloroethylene increases.

Let us examine other possible paths yielding 1,1-dichloroethylene. Tschuikow-Roux *et al.*[15] found $CF_2{=}CH_2$ besides the main product $CHF{=}CH_2$ in their shock tube study of CHF_2CH_3. They suggested the following reactions for the formation of $CF_2{=}CH_2$;

$$\mathrm{CH_3\cdot} + \mathrm{CH_3CHF_2} \longrightarrow \mathrm{CH_3CF_2\cdot} + \mathrm{CH_4}, \qquad (25)$$

$$2\mathrm{CH_3CF_2\cdot} \longrightarrow \mathrm{CF_2{=}CH_2} + \mathrm{CH_3CHF_2}. \qquad (26)$$

In the present case, 1,1-dichloroethylene may be produced by the following reactions analogous to Reactions 25 and 26;

$$\mathrm{CDCl_2\cdot}\ (\text{or } \mathrm{CH_3\cdot}) + \mathrm{CH_3CDCl_2} \longrightarrow$$
$$\mathrm{CH_3CCl_2\cdot} + \mathrm{CD_2Cl_2}\ (\text{or } \mathrm{CH_3D}), \qquad (27)$$

$$2\mathrm{CH_3CCl_2\cdot} \longrightarrow \mathrm{CH_2{=}CCl_2} + \mathrm{CH_3CHCl_2}. \qquad (28)$$

In the present experiment, however, neither dichloroethane nor dichloromethane was found in the products. This indicates that Reactions 27 and 28 are not important for the formation of dichloroethylene. Next, let us consider the disproportionation of the $CDCl_2$ radical;

$$2\mathrm{CDCl_2\cdot} \longrightarrow \mathrm{CD_2Cl_2} + \mathrm{CCl_2{:}}, \qquad (29)$$

$$\mathrm{CCl_2{:}} + \mathrm{CH_3\cdot} \longrightarrow \mathrm{CH_3CCl_2\cdot}^* \longrightarrow \mathrm{CH_2{=}CCl_2} + \mathrm{H\cdot}. \qquad (30)$$

These reactions would produce a considerable amount of dichloromethane, which also is not compatible with the above observation. Therefore, it may be concluded that Reaction 24 is the most probable process for yielding dichloroethylene.

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References

1) G. P. Semeluk and R. B. Bernstein, *J. Am. Chem. Soc.*, **75**, 3793 (1954); G. P. Semeluk and R. B. Bernstein, *ibid.*, **79**, 46 (1957).

2) A. E. Shilov and R. D. Sabirova, *Zh. Fiz. Khim.*, **34**, 860 (1960).

3) M. Tsuda and K. Kuratani, *Bull. Chem. Soc. Jpn.*, **41**, 53 (1968).

4) T. Yano, *Bull. Chem. Soc. Jpn.*, **46**, 1619 (1973).

5) All the chlorinated ethanes except the penta- and hexa-substituted ones were analyzed; only 1,1,2,2-tetrachloroethane was found in Series I, while 1,1,2,2-tetrachloroethane and ethyl chloride were found in Series II.

6) As can be seen from Figs. 1 and 2, the ratios among the main-product yields show little change in the range of conversion below 50%. This suggests that the same reaction mechanism is operative. When the conversions are reduced to the reaction temperatures, a wide conversion range corresponds to a very narrow temperature range, for example, a 20% conversion to less than 50 K. A change in mechanism is not likely to occur in this narrow temperature range. Therefore, the conversion may be regarded as the extent of the reaction in such a narrow temperature range.

7) In the case of the II series, dichloromethane is produced, but it seems to disappear at higher temperatures (Fig. 1). Therefore, the following secondary reactions may be supposed;

$$\mathrm{CHDCl_2} + \text{radical}(\mathrm{R\cdot})\ \text{or atom}(\mathrm{X\cdot}) \longrightarrow$$
$$\mathrm{CDCl_2\cdot} + \mathrm{RH}\ \text{or}\ \mathrm{XH},$$

$$\mathrm{CDCl_2\cdot + CHCl_2\cdot \longrightarrow CDCl_2CHCl_2^* \longrightarrow C_2DCl_3 + HCl.}$$

8) M. J. Perona, J. T. Bryant, and G. O. Pritchard, *J. Am. Chem. Soc.*, **90**, 4782 (1968).

9) K. C. Kim, D. W. Setser, and B. E. Holmes, *J. Phys. Chem.*, **77**, 725 (1973).

10) K. C. Kim and D. W. Setser, *J. Phys. Chem.*, **76**, 283 (1972); K. C. Kim and D. W. Setser, *ibid.*, **78**, 2166 (1974).

11) S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965).

12) The change in the internal energy with the temperature was calculated from $C_v^{vib}(T-298)=3R(T-298)+[C_v^{vib}$, $\mathrm{CDCl_2}(T)+C_v^{vib}$, $\mathrm{CH_3}(T)]T-[C_v^{vib}$, $\mathrm{CDCl_2}(298)+C_v^{vib}$, $\mathrm{CH_3}(298)]298$. The same value of C_v^{vib} was assumed for $CDCl_2$ and $CHCl_2$. The vibrational contributions to the heat capacities of $CHCl_2$ and CH_3 were estimated from the heat capacities of CH_2Cl_2 and CH_3 respectively.

13) J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3246 (1966).

14) In order to explain the greatest yield of 1,1-dichloroethylene, the change in the C_1 radical distribution due to the following hydrogen metathesis reactions are considered;

$$\mathrm{CDCl_2\cdot + CH_4 \longrightarrow CH_3\cdot + CHDCl_2,}$$

$$\mathrm{CDCl_2\cdot + CDCl_3 \longrightarrow CCl_3\cdot + CD_2Cl_2.}$$

However, the contributions of these reactions can be neglected for two reasons. The first is that there is no detectable amount of dichloromethane. The second is the kinetic one. Assuming the steady-state and the same recombination rate constants of the C_1 radicals, the steady-state rate is concluded to be considerably faster than that of the transformation among C_1 radicals. Thus, the disturbance of the C_1 radical distribution due to the above reactions is insignificant.

15) E. Tschuikow-Roux, W. J. Quiring, and J. M. Simmie, *J. Phys. Chem.*, **74**, 2449 (1970).