A Systematic Study of the Yields of γ-Radiolysis Products in C_1, C_2, and C_3-Chlorofluorocarbons

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In the presence of bromine as a scavenger, the yields of the radiolysis products in eleven kinds of C_1—C_3 chlorofluorocarbons were investigated by means of gas chromatography. The *G*-values for the rupture of bonds in radiolysis were found to correlate with the halogen composition and the structure of their molecules. The *G*-values for the C–Cl (or C–F) bond rupture generally appear to increase with the number of chlorine (or fluorine) atoms in the chlorofluorocarbons; there was a marked difference between the *G*-values for the C–Cl rupture in each pair of structural isomers of chlorofluoroethanes. A striking selectivity in bond rupture was observed between the two C–C bonds in the chlorofluoropropanes.

Although the chlorofluorocarbons with three different types of bonds are interesting sytsems in radiation chemistry, only one work on the radiolysis of $CF_2ClCFCl_2$ (without scavengers) had been reported[1)] before we initiated a systematic investigation of the radiolysis of chlorofluorocarbons as a preliminary step to the study of the radiolysis and radiation synthesis of various inorganic mixed halides. Our previous work on CF_2Cl_2, $CFCl_3$, CF_2ClCF_2Cl, and $CF_2ClCFCl_2$ with bromine as the scavenger, has revealed that the C–Cl and C–C bonds are generally more reactive than the C–F bond in the radiolysis reactions.[2,3)] Recently we have studied the yields of the radiolysis products in C_1—C_3 chlorofluorocarbons and found that the reactivities of such bonds are largely influenced by the number of chlorine atoms and the structure concerning the C–Cl bonding in the molecule.[4,5)] The object of the present article is to report the systematics in the reactivities of such bonds, derived from a detailed analysis of our recent data on the *G*-values of radiolysis products in the C_1, C_2, and C_3-chlorofluorocarbons, since the knowledge of the reactivities of the bonds in these compounds appears to be useful for elucidation of the mechanisms of radiolytic reactions and for the selection of procedures for the radiation synthesis of mixed halocarbons.

Experimental

Materials. Eleven kinds of chlorofluorocarbons were studied in the present work. Of these, CCl_4, $CFCl_3$, CF_2Cl_2, CF_2ClCF_2Cl, $CF_2ClCFCl_2$, and $CFCl_2CFCl_2$ were purchased from the Tokyo Chemical Industry Co., and CF_3CFCl_2, CF_3CCl_3, CF_2ClCCl_3, $CF_3CFClCF_2Cl$, and $CF_3CF_2CCl_3$, from P C R, Inc., U.S.A.; all were of a guaranteed reagent grade. These chlorofluorocarbons were purified three times by trap-to-trap distillation before use. The samples for γ-irradiation (all as liquid) were prepared by condensing mixtures of a chlorofluorocarbon and bromine into quartz capillary ampoules on a greaseless vacuum system equipped with Teflon needle valves. The bromine in the mixtures was determined by radioactivation analysis with thermal neutrons (15-s irradiation at a flux of 5×10^{11} n/cm^2 s).[6)]

Gamma-ray Irradiation. The γ-irradiations were performed in a 16000-Ci ^{60}Co source for 5 to 25 h at an ambient temperature. The dose rates at the irradiation site were in the range of 2.27×10^{18}—2.73×10^{18} eV/g min, and the total energy absorbed in the system (0.82×10^{21}—3.40×10^{21} eV/g) was estimated on the basis of the electron densities of these compounds.

Gas Chromatographic Analysis of the γ-Irradiated Samples. The γ-irradiated samples were directly introduced into a gas chromatograph equipped with a thermal conductivity detector. The inorganic halogen in the mixtures was removed by means of a short stripping column packed with dehydrated potassium ferrocyanide powder, and then the organic species were analyzed on a 5-m Silicone DC 550 column. The unknown peaks on the gas chromatogram were mainly identified by (1) comparing their retention times with those of known compounds, or (2) by utilizing the known correlation between the logarithm of the retention volume and the composition of halogen atoms in mixed halocarbons.[7–9)] Whenever it became necessary to confirm the identity of peaks of bromine-containing organic species, the γ-irradiated samples were further activated with thermal neutrons and their radiogas chromatograms were obtained by means of counting the ^{82}Br activities with an external γ-ray detector (NaI scintillation counter) placed after the thermal conductivity detector. The quantities of the products were determined from the TCD peak areas corrected for the detector sensitivities which had been obtained experimentally.[10)]

Results and Discussion

Radiolysis of $CF_2ClCFCl_2$. Of the eleven chlorofluorocarbons studied in the present work, the radiolysis of $CF_2ClCFCl_2$ will be described here in detail as a typical example. In the presence of bromine, the major radiolysis products from $CF_2ClCFCl_2$ are $C_2F_3Cl_2Br$, CF_2ClBr, $CFCl_2Br$, and $C_2F_3ClBr_2$, which may be derived from the C–Cl and C–C bond rupture of the parent compound, followed by scavenging with bromine. The concentrations of the major products show a linear dose-dependence for the irradiation conditions used in this work (Fig. 1). The conversion of the parent compound was about 5% for a 10-h irradiation. As is illustrated in Fig. 2, the yields (in terms of *G*-values) of the bromine-scavenged products increase sharply with the increase in the bromine concentration and nearly level off at 0.1—0.2 mole fraction bromine. Table 1 summarizes the *G*-values for the formation of the major radiolysis products obtained from the plateau values of such scavenger curves. We can estimate, for example, the *G*-values for the rupture of the C–Cl or C–C bond on the assumption that the plateau *G*-value of $C_2F_3Cl_2Br$ or CF_2-

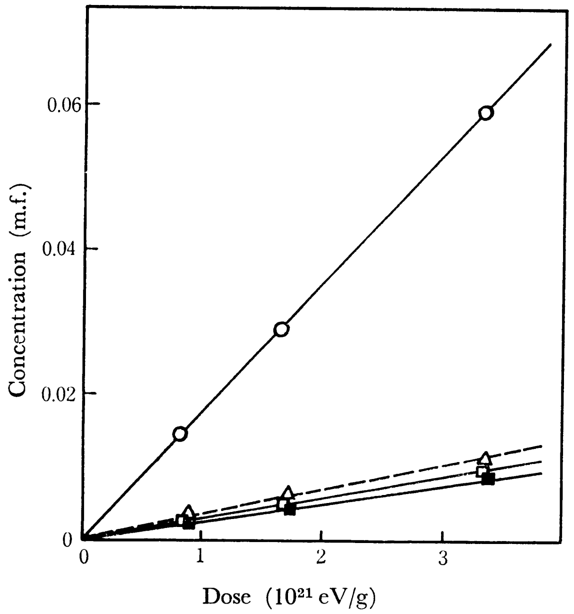

Fig. 1. The dose-dependence of the major radiolysis products from $CF_2ClCFCl_2$ containing 0.1 m. f. Br_2. —○— $C_2F_3Cl_2Br$; —□— CF_2ClBr; —■— $CFCl_2Br$; --△-- $C_2F_3ClBr_2$.

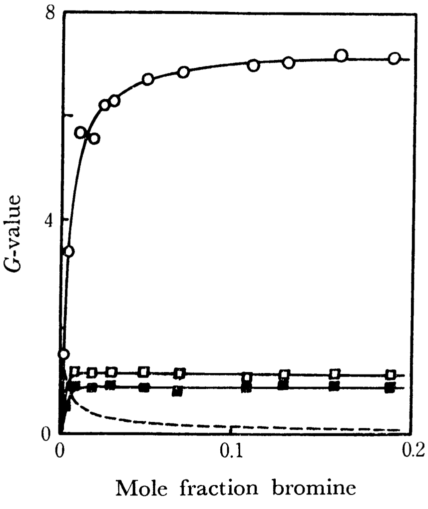

Fig. 2. The G-values for formation of major radiolysis products in the $CF_2ClCFCl_2$-Br_2 system as a function of bromine concentration.
—○— $C_2F_3Cl_2Br$; —□— CF_2ClBr; —■— $CFCl_2Br$; ---- CF_2Cl_2, $CFCl_3$

ClBr (or $CFCl_2Br$) corresponds to the G-value for the formation of the $C_2F_3Cl_2$ or CF_2Cl (or $CFCl_2$) radical (Table 1). Although the C_3 and C_4-chlorofluorocarbons resulting from the recombination or cross-combination of such radicals disappear quickly in the presence of bromine, the yields of CF_2Cl_2 and $CFCl_3$ decrease somewhat slowly with the increase in the bromine concentration (Fig. 2). The latter observation indicates that the chlorine accumulated in the system as the result of the C–Cl rupture during radiolysis may possibly compete with bromine for combination with the CF_2Cl and $CFCl_2$ radicals, thereby slightly reducing the bromine-scavenging effect on the formation of CF_2Cl_2 and $CFCl_3$.

Table 1. G-values for the formation of the major radiolysis products in liquid $CF_2ClCFCl_2$ containing bromine

Product	Bond ruptured	G-value[a,b]
$C_2F_3Cl_2Br$	C-Cl	7.0 ±0.3
$CFCl_2Br$[c]	C-C	1.0 ±0.1
CF_2ClBr[c]	C-C	
$C_2F_3ClBr_2$	two C-Cl	1.3 ±0.1
$C_2F_2Cl_3Br$	C-F	0.16±0.01

a) G-value obtained at the plateau of the bromine-scavenger cure. b) Small amounts (G-value<0.1) of CF_2Br_2 and $CFClBr_2$, possibly derived from the rupture of both C-C and C-Cl bonds were also observed. c) The G-values for the formation of $CFCl_2Br$ and CF_2ClBr were 0.9 and 1.1 respectively.

The rupture of the single C–Cl bond in $CF_2ClCFCl_2$ can produce either of two isomers of $C_2F_3Cl_2Br$, *i.e.*, $CF_2ClCFClBr$ or $CF_2BrCFCl_2$. Although they could not be separated from each other by gas chromatography, the comparison of the yields of radiolysis products obtained from the re-irradiation of the $C_2F_3Cl_2Br$ fraction implies that the C(1)–Cl bond rupture was preferred by a factor of 3—4 to the C(2)–Cl bond rupture (the positions of carbon atoms are defined in the footnote to Table 2).

The product, $C_2F_3ClBr_2$, corresponding to the rupture of the two C–Cl bonds may not arise from the successive radiolysis process: $C_2F_3Cl_3+Br_2 \rightsquigarrow C_2F_3Cl_2Br$ and $C_2F_3Cl_2Br+Br_2 \rightsquigarrow C_2F_3ClBr_2$, since the G-value estimated for such a process can account for only a minor fraction of the observed G-value. It is likely that this product is mainly formed through the nearly simultaneous elimination of two chlorine atoms from adjacent carbon atoms (leading to the formation of an olefinic bond) and combination with bromine.[11]

Systematic Comparison of the G-values in C_1—C_3 Chlorofluorocarbons. Similar types of reactions and scavenging effects were observed for all the C_1—C_3 chlorofluorocarbons studied in the present work. In Table 2 are summarized the G-values for the rupture of various bonds, as estimated from the plateau G-values of the corresponding bromine-scavenged products, as has been described above.

The intra- and intermolecular comparison of the results listed in Table 2 indicates that the G-values for bond rupture in the C_1—C_3 chlorofluorocarbons tend to increase in the order: C–F<C–C<C–Cl, which is in accordance with the decreasing order of the bond dissociation energies of such bonds. Hence, we may consider that, in general, the weaker bond is more reactive. However, a more detailed analysis indicates that the G-values depend on the halogen composition and the structure of the parent molecules, as will be discussed below.

C–F Bond Rupture: For the compounds containing the same number of carbon atoms, the G-value for the C–F rupture tends to increase with the number of fluorine atoms in the molecule (Fig. 3). While there

Table 2. G-values for rupture of various bonds in chlorofluorocarbons

No.	Compound	G-values for bond rupture[10)]				
		C-Cl rupture	Double C-Cl rupture	C-F rupture	C(1)-C(2) rupture[a,b)]	C(2)-C(3) rupture[a,b)]
1	CF_2Cl_2	6.7	0.8	0.20		
2	$CFCl_3$	8.1	1.0	0.05		
3	CCl_4	7.7	0.3_3			
4	CF_3CFCl_2 (1,1-dichloro-)	5.9	0.15	0.5_1	1.0	1.0
5	CF_2ClCF_2Cl (1,2-dichloro-)	5.1	0.4_4	0.5_2	0.8	
6	CF_3CCl_3 (1,1,1-trichloro-)	9.3	0.3_1	0.15	0.9	
7	$CF_2ClCFCl_2$ (1,1,2-trichloro-)	7.0	1.3	0.16	1.0	
8	CF_2ClCCl_3 (1,1,1,2-tetrachloro-)	7.9	1.6	0.14	1.2	
9	$CFCl_2CFCl_2$ (1,1,2,2-tetrachloro-)	6.6	2.4	0.11	1.3	
10	$CF_3CFClCF_2Cl$ (1,2-dichloro-)	4.8	0.6_4	0.6_2	1.4	0.16
11	$CF_3CF_2CCl_3$ (1,1,1-trichloro-)	8.5	0.17	0.18	0.9	0·08

a) The positions of the carbon atoms are defined in the present article as follows: $CF_3CFClCF_2Cl$ as 1,2-dichlorohexafluropropane, and $CF_3CF_2CCl_3$ as 1,1,1-trichloropentafluoropropane. b) The G-values for the formation of the C-C scission products are as follows: CF_3Br (1.4) and $CFCl_2Br$ (0.6) from CF_3CFCl_2; CF_2ClBr (1.5) from CF_2ClCF_2Cl; CF_3Br (0.8) and CCl_3Br (1.0) from CF_3CCl_3; CF_2ClBr (1.1) and $CFCl_2Br$ (0.9) from $CF_2ClCFCl_2$; CF_2ClBr (1.2) and CCl_3Br (1.3) from CF_2ClCCl_3; $CFCl_2Br$ (2.6) from $CFCl_2CFCl_2$; $CF_3CFClBr$ (1.4) and $CF_2ClCFClBr$ (0.16) from $CF_3CFClCF_2Cl$; CCl_3Br (0.9) and CCl_3CF_2Br (0.08) from $CF_3CF_2CCl_3$. The values for the other products (CF_3Br, CF_2ClBr, and CF_3CF_2Br) from chlorofluoropropanes were omitted because, for analytical reasons, they could not be determined accurately.

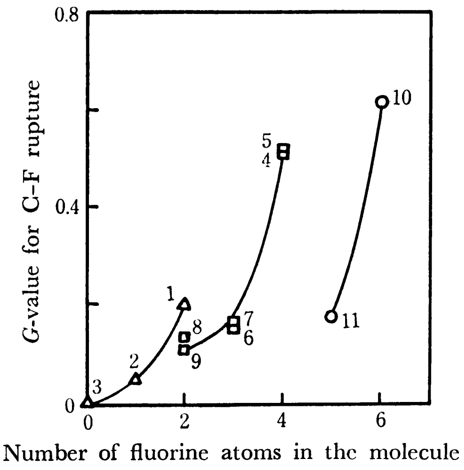

Fig. 3. The G-values for the C-F rupture as a function of the number of fluorine atoms in chlorofluoromethanes(△), chlorofluoroethanes(□), and chlorofluoropropanes(○).
(Keys to the numbers denoting compounds in Figs. 3—5 are given in Table 2).

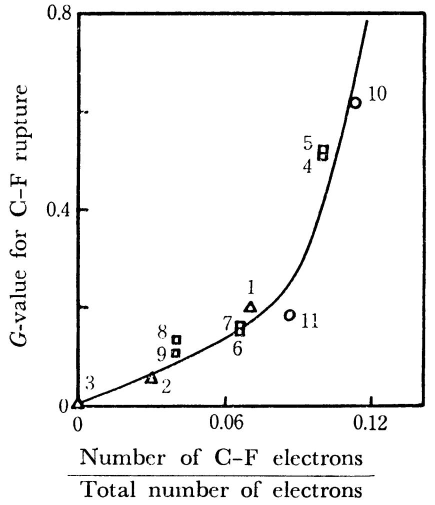

Fig. 4. The G-values for the C-F rupture as a function of the ratio of the number of electrons involved in the C-F bonding to the total number of electrons in the molecules of chlorofluoromethanes(△), chlorofluoroethanes(□), and chlorofluoropropanes(○).

are three isomeric pairs of chlorofluoroethanes, no significant difference was observed between the G-values for each pair of isomers. In Fig. 4, the G-value for the C–F rupture appears to correlate with the ratio of the number of electrons involved in the C–F bonding to the total number of electrons in the molecule. Thus, it is likely that the mechanism for the rupture of stable C–F bonds is possibly governed by a direct process, irrespective of small differences in the bond dissociation energies or structures of the molecules.

C-Cl Bond Rupture: As may be seen in Fig. 5, the G-value for the C–Cl rupture tends to increase slightly

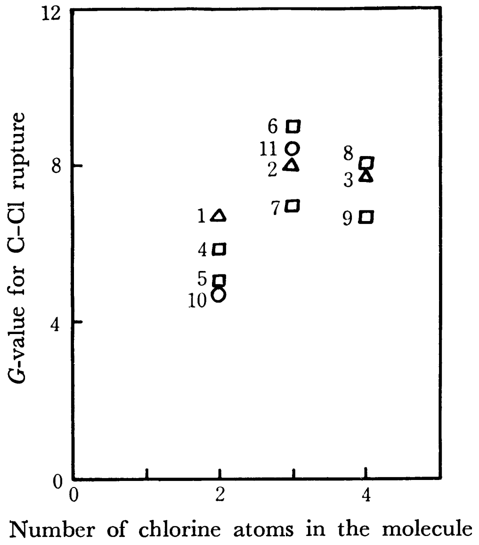

Fig. 5. The G-values for the C-Cl rupture as a function of the number of chlorine atoms in chlorofluoromethanes(△), chlorofluoroethanes(□), and chlorofluoropropanes(○).

with the number of chlorine atoms in the molecules containing the same number of carbon atoms, except for $CFCl_2CFCl_2$ and CF_2ClCCl_3. The difference between the G-values for each pair of isomers is large, and the isomer with a more asymmetrical structure concerning the C–Cl bonding (in which all or most chlorine atoms are bonded to one carbon atom) always gives a higher G-value for the C–Cl rupture. Such a trend may be accounted for tentatively by assuming that (1) the C–Cl bond dissociation energy may be slightly decreased with the increase in the total number of chlorine atoms in the molecule,[12] and that (2) the instability of the C–Cl bonding may be increased with the number of chlorine atoms attached to the same carbon atom as a result of the increased strain. When the G-value for the C–Cl rupture was plotted against the ratio of the number of electrons involved in the C–Cl bonding to the total number of electrons in the molecule, the correlation was not clear and was quite different from that observed for the C–F rupture in Fig. 4. Hence, the mechanism leading to the C–Cl rupture may be possibly controlled by processes which can be affected by small differences in the bond dissociation energies and structures of the molecules. While the radiolysis products in these systems are generally accountable in terms of the free radical processes, at least as intermediate steps, we should also examine the possibility that the dissociative electron attachment process involving electrons at low energies may contribute to the formation of such radicals (R):

$$RCl + e^- \longrightarrow R + Cl^-$$

However, only a few data on the dissociative attachment cross sections in the gas phase are available,[13] and the correlation between the G-value for the C–Cl rupture and the cross section for such a process in the liquid phase is still ambiguous.[14]

Besides the rupture of the single C–Cl bond, two C–Cl bonds in a molecule were often found to break, although the G-values for such a double C–Cl rupture were much smaller than for the single C–Cl rupture. For the chlorofluoroethanes, there is a marked difference between the G-values for each pair of isomers: in contrast to the single C–Cl rupture, the G-value is always larger for the symmetrical or less asymmetrical isomer (*i.e.*, 1,2-dichloro-, 1,1,2-trichloro-, and 1,1,2,2-tetrachloro-) than for the more asymmetrical counterpart (*i.e.*, 1,1-dichloro-, 1,1,1-trichloro-, and 1,1,1,2-tetrachloro-). Thus, the difference in the G-values for the single C–Cl rupture between the pair of isomers may be partly accounted for by the inverse difference in the G-values for the double C–Cl rupture. While the G-value for the double C–Cl rupture increases with the number of chlorine atoms in the series of the symmetrical or less asymmetrical isomers, it remains at low values in the series of the more asymmetrical isomers, except for the case of CF_2ClCCl_3. As has been indicated earlier, the large G-values for the double C–Cl rupture of the symmetrical and less asymmetrical isomers may be mainly ascribed to the nearly simultaneous elimination of two chlorine atoms from the adjacent carbon atoms, whereas the origin of the products corresponding to the double C–Cl rupture in the more asymmetrical isomers can be explained in terms of the successive radiolysis processes *via* monobromo compounds as intermediates (the simultaneous elimination process can also take place in CF_2ClCCl_3). These observations indicate that the G-values for the rupture of one or two C–Cl bonds in the chlorofluorocarbons are influenced by the number of chlorine atoms and the structure in the molecule: for the chlorofluorethanes and chlorofluoropropanes, the single C–Cl rupture occurs predominantly in the more asymmetrical isomers, while the double C–Cl rupture takes place appreciably in the symmetrical and less asymmetrical isomers.

C–C Bond Rupture: The G-values for the C(1)–C(2) rupture in the chlorofluoroethanes remain almost unchanged, or they increase only slightly with the increase in the number of chlorine atoms in the molecule; yet no significant difference is observed between the pair of isomers.

However, a striking selectivity in bond rupture is observed between the two C–C bonds in the chlorofluoropropanes: the G-values for the C(1)–C(2) rupture are about ten times those for the C(2)–C(3) rupture. Such a marked weakness of the C(1)–C(2) bond may be tentatively accounted for by the greater resonance stabilization obtainable in the formation of the C(1)–C(2) scission products than the C(2)–C(3) scission products.

a) In the case of $CF_3CF_2CCl_3$, the C(1)–C(2) rupture eventually yields CF_3CF_2 and CCl_3 radicals, while the C(2)–C(3) rupture produces CCl_3CF_2 and CF_3 radicals. The CCl_3 radical is near planar,[15] while the CF_3 radical has a deep pyramidal structure.[16] Thus, the strain energy in the ground state due to the proximity of halogen atoms in trihalomethyl groups may be more released in the formation of $\cdot CCl_3$ than in the formation of $\cdot CF_3$. This difference in shape between the two radicals may also lead to the larger interaction between the lone pair on halogen and the p-orbital of carbon in the CCl_3 radical than in the CF_3 radical. Accordingly, a greater resonance stabilization may be acquired in the formation of $\cdot CCl_3$; thus, the C(1)–C(2) rupture will be favored. In addition, the steric interaction between the Cl atoms on C(1) and the F atoms on C(2) may elongate the C(1)–C(2) bond length and somewhat weaken the bond strength as compared with that of the C(2)–C(3) bond.

b) In $CF_3CFClCF_2Cl$, the C(1)–C(2) scission produces $CF_3CFCl\cdot$ and $\cdot CF_2Cl$, while the C(2)–C(3) scission yields $CF_2ClCFCl\cdot$ and $\cdot CF_3$. Since a greater resonance stabilization may be expected for the $\cdot CF_2Cl$ formation than for the $\cdot CF_3$ formation, the C(1)–C(2) rupture is favored. The elongation of the C(1)–C(2) bond as a result of the steric interaction between the Cl atoms on C(1) and C(2) atoms also tends to weaken the C(1)–C(2) bond.

In conclusion, the *G*-values for the rupture of various bonds in the chlorofluorocarbons are generally influenced by the halogen composition and the structure of the molecule. The systematic investigation of the *G*-values and the selectivity in bond rupture may provide us with important clues to an understanding of the mechanisms of radiolytic reactions as well as to establishing the systematics in radiation synthesis. Moreover, the present results may afford useful knowledge on the chemical reactivities of chlorofluorocarbons, which have not been fully studied in organic chemistry.

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10) Since the sensitivity in the thermal conductivity detector appeared to correlate with the molecular weight for some chlorofluorocarbons, the sensitivities of most radiolysis products were estimated in our previous work by extrapolation based on such a correlation.[3–5] However, more extensive measurements of a number of bromochlorofluorocarbons have recently been carried out in our laboratory, and most bromine-containing compounds have been found to deviate appreciably from the above correlation (the details will be published elsewhere). Accordingly, the new sensitivity data determined experimentally have been used in the present work to re-calculate the *G*-values of the radiolysis products instead of the previous data mainly estimated by extrapolation.

11) The ^{19}F NMR spectrum of the $C_2F_3ClBr_2$ fraction revealed that $CF_2BrCFClBr$ was the predominant species.

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14) On a hypothetical assumption that the ratio of the cross sections of the two chlorofluorocarbons in the liquid phase is similar to that in the gas phase, the dissociative attachment cross section of $CFCl_3$ may be about 100 times as large as that of CF_2Cl_2, whereas the difference in the *G*-values for the C–Cl rupture between these compounds is relatively small (1.4). Thus it seems unlikely that the dissociative electron attachment is the major process controlling the C–Cl bond rupture.

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