Ab initio study of reactions between halogen atoms and various fuel molecules by Gaussian-2 theory

Shigeo Kondo *, Kazuaki Tokuhashi, Akifumi Takahashi, Masahiro Kaise

National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki 305-0046 Japan

Abstract

Ab initio calculations by using Gaussian-2 theory have been carried out for the reactions between halogen atoms and various fuel molecules, i.e. fluorine, chlorine, and bromine atoms vs. hydrogen, methane, ethane, ethylene, acetylene, ammonia, silane, dichlorosilane and phosphine. The activation energy for the reaction between a halogen atom and a fuel molecule seems to indicate whether the reaction between the fuel gas and the corresponding halogen gas occurs spontaneously when they are brought into contact to each other at room temperature. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Fluorine gas is known to be extremely reactive. It may react immediately with any kind of fuel gas at room temperature and may in some cases cause explosion. Chlorine and bromine are not so reactive as fluorine, but are still very reactive against various kinds of chemicals. Yet it is not necessary that any combination of halogen and fuel gases react spontaneously at room temperature. From a safety point of view, it is very important to know which halogen gas reacts readily with what kind of fuel gas at room temperature [1–3].

---

* Corresponding author. Tel.: +81-298-61-4770; fax: +81-298-54-4487.
E-mail address: kondo@nimc.go.jp (S. Kondo).

Table 1
Geometrical parameters of the transition states of reactions between halogen atoms and fuel molecules[a]

Reaction	Geometry
(1) $F + H_2$	$H_1H_2 = 0.7991$, $H_2F = 1.3217$, $aH_1H_2F = 180.00$
(2) $F + CH_4$	$CH_1 = 1.1533$, $CH_2 = CH_3 = CH_4 = 1.0874$, $H_1F = 1.3498$, $aH_1CH_2 = aH_1CH_3 = aH_1CH_4 = 106.74$, $aCH_1F = 180.00$, $bH_3CH_1H_2 = -bH_4CH_1H_2 = 120.00$
(3) $F + C_2H_6$	$C_1C_2 = 1.5140$, $C_1H_1 = 1.0934$, $C_1H_2 = C_1H_3 = 1.0914$, $C_2H_4 = 1.1435$, $C_2H_5 = C_2H_6 = 1.0916$, $H_4F = 1.4139$, $aC_2C_1H_1 = 110.51$, $aC_2C_1H_2 = aC_2C_1H_3 = 110.98$, $aC_1C_2H_4 = 109.69$, $aC_1C_2H_5 = aC_1C_2H_6 = 113.24$, $aC_2H_4F = 150.81$, $bH_2C_1C_2H_1 = -bH_3C_1C_2H_1 = 110.98$, $bH_4C_2C_1H_1 = 180.00$, $bH_5C_2C_1H_1 = -bH_6C_2C_1H_1 = 63.07$, $bFH_4C_2C_1 = 0.00$
(4) $F + C_2H_4$	$C_1C_2 = 1.3557$, $C_2F = 1.8407$, $C_1H_1 = C_1H_2 = 1.0803$, $C_2H_3 = C_2H_4 = 1.0815$, $aC_1C_2F = 73.36$, $aC_2C_1H_1 = aC_2C_1H_2 = 121.23$, $aC_1C_2H_3 = aC_1C_2H_4 = 121.25$, $bH_1C_1C_2F = -bH_2C_1C_2F = 91.01$, $bH_3C_2C_1F = -bH_4C_2C_1F = 93.45$
(5) $F + C_2H_2$	$C_1C_2 = 1.1956$, $C_2F = 1.9071$, $C_1H_1 = 1.0653$, $C_2H_2 = 1.0655$, $aC_1C_2F = 89.92$, $aC_2C_1H_1 = 175.39$, $aC_1C_2H_2 = 169.84$, $bH_1C_1C_2F = 0.00$, $bH_2C_2C_1F = 180.00$
(6) $F + NH_3$	$NH_1 = 1.0334$, $H_1F = 1.5243$, $NH_2 = NH_3 = 1.0109$, $aNH_1F = 99.14$, $aH_1NH_2 = aH_1NH_3 = 113.92$, $bH_2NH_1F = -bH_3NH_1F = 66.25$
(7) $F + SiH_4$	$SiH_1 = 1.8132$, $SiH_2 = 1.4940$, $SiH_3 = SiH_4 = 1.4772$, $H_1F = 1.1820$, $aH_1SiH_2 = 102.82$, $aH_1SiH_3 = 119.45$, $aH_1SiH_4 = 106.24$, $aSiH_1F = 78.48$, $bH_3SiH_1H_2 = 117.21$, $bH_4SiH_1H_2 = -114.02$, $bFH_1SiH_2 = 196.43$
(8) $F + SiH_2Cl_2$	$SiH_1 = 1.8552$, $SiH_2 = 1.4695$, $SiCl_1 = 2.0558$, $SiCl_2 = 2.0365$, $H_1F = 1.1320$, $aH_1SiH_2 = 123.29$, $aH_1SiCl_1 = 107.79$, $aH_1SiCl_2 = 103.89$, $aSiH_1F = 76.69$, $bCl_1SiH_1H_2 = 119.62$, $bCl_2SiH_1H_2 = -121.83$, $bFH_1SiH_2 = 22.20$
(9) $F + PH_3$	$PH_1 = 1.4414$, $H_1F = 1.5910$, $PH_2 = PH_3 = 1.4119$, $aPH_1F = 137.82$, $aH_1PH_2 = aH_1PH_3 = 95.57$, $bH_2PH_1F = 47.69$, $bH_3PH_1F = -47.73$
(10) $Cl + H_2$	$H_1H_2 = 0.9533$, $H_2Cl = 1.4601$, $aH_1H_2Cl = 180.00$
(11) $Cl + CH_4$	$CH_1 = 1.4376$, $CH_2 = CH_3 = CH_4 = 1.0843$, $H_1Cl = 1.4306$, $aH_1CH_2 = aH_1CH_3 = aH_1CH_4 = 101.17$, $aCH_1Cl = 180.00$, $bH_3CH_1H_2 = -bH_4CH_1H_2 = 120.00$
(12) $Cl + C_2H_6$	$C_1C_2 = 1.4964$, $C_1H_1 = 1.0976$, $C_1H_2 = C_1H_3 = 1.0916$, $C_2H_4 = 1.4246$, $C_2H_5 = C_2H_6 = 1.0881$, $H_4Cl = 1.4410$, $aC_2C_1H_1 = 109.75$, $aC_2C_1H_2 = aC_2C_1H_3 = 111.42$, $aC_1C_2H_4 = 104.62$, $aC_1C_2H_5 = aC_1C_2H_6 = 117.44$, $aC_2H_4Cl = 178.25$, $bH_2C_1C_2H_1 = -bH_3C_1C_2H_1 = 119.21$, $bH_4C_2C_1H_1 = 180.00$, $bH_5C_2C_1H_1 = -bH_6C_2C_1H_1 = 70.83$, $bClH_4C_2C_1 = 0.00$
(13) $Cl + C_2H_4$	$C_1C_2 = 1.3453$, $C_2Cl = 2.3801$, $C_1H_1 = C_1H_2 = 1.0827$, $C_2H_3 = C_2H_4 = 1.0828$, $aC_1C_2Cl = 89.68$, $aC_2C_1H_1 = aC_2C_1H_2 = 121.35$, $aC_1C_2H_3 = aC_1C_2H_4 = 121.22$, $bH_1C_1C_2Cl = -bH2C_1C_2Cl = 88.31$, $bH_3C_2C_1Cl = -bH_4C_2C_1Cl = 95.46$
(14) $Cl + C_2H_2$	$C_1C_2 = 1.2071$, $C_2Cl = 2.2112$, $C_1H_1 = 1.0664$, $C_2H_2 = 1.0688$, $aC_1C_2Cl = 105.85$, $aC_2C_1H_1 = 171.25$, $aC_1C_2H_2 = 156.69$, $bH_1C_1C_2Cl = 0.00$, $bH_2C_2C_1Cl = 180.00$
(15) $Cl + NH_3$	$NH_1 = 1.2990$, $H_1Cl = 1.4698$, $NH_2 = NH_3 = 1.0257$, $aNH_1Cl = 150.56$, $aH_1NH_2 = aH_1NH_3 = 108.76$, $bH_2NH_1Cl = -bH_3NH_1Cl = 57.97$
(16) $Cl + SiH_4$	$SiH_1 = 1.6590$, $SiH_2 = SiH_3 = SiH_4 = 1.4785$, $H_1Cl = 1.5790$, $aH_1SiH_2 = aH_1SiH_3 = aH_1SiH_4 = 106.40$, $aSiH_1Cl = 180.00$, $bH_3SiH_1H_2 = -bH_4SiH_1H_2 = 120.00$
(17) $Cl + SiH_2Cl_2$	$SiH_1 = 1.6492$, $SiH_2 = 1.4751$, $SiCl_1 = SiCl_2 = 2.0276$, $H_1Cl_3 = 1.5694$, $aH_1SiH_2 = 108.75$, $aH_1SiCl_1 = aH_1SiCl_2 = 107.31$ $aSiH_1Cl_3 = 176.64$, $bCl_1SiH_1H_2 = -bCl_2SiH_1H_2 = 119.65$, $bCl_3H_1SiH_2 = 0.0$

Table 1 (*continued*)

Reaction	Geometry
(18) $Cl + PH_3$	$PH_1 = 1.4942$, $H_1Cl = 1.7574$, $PH_2 = PH_3 = 1.4134$, $aPH_1Cl = 158.40$, $aH_1PH_2 = aH_1PH_3 = 95.23$, $bH_2PH_1Cl = 47.49$, $bH_3PH_1Cl = -47.58$
(19) $Br + H_2$	$H_1H_2 = 1.0876$, $H_2Br = 1.5423$, $aH_1H_2Br = 180.00$
(20) $Br + CH_4$	$CH_1 = 1.6027$, $CH_2 = CH_3 = CH_4 = 1.0828$, $H_1Br = 1.5261$, $aH_1CH_2 = aH_1CH_3 = aH_1CH_4 = 99.22$, $aCH_1Br = 180.00$, $bH_3CH_1H_2 = -bH_4CH_1H_2 = 120.00$
(21) $Br + C_2H_6$	$C_1C_2 = 1.4923$, $C_1H_1 = 1.0983$, $C_1H_2 = C_1H_3 = 1.0919$, $C_2H_4 = 1.6302$, $C_2H_5 = C_2H_6 = 1.0863$, $H_4Br = 1.5200$, $aC_2C_1H_1 = 110.27$, $aC_2C_1H_2 = aC_2C_1H_3 = 111.35$, $aC_1C_2H_4 = 101.14$, $aC_1C_2H_5 = aC_1C_2H_6 = 118.79$, $aC_2H_4Br = 173.52$, $bH_2C_1C_2H_1 = -bH_3C_1C_2H_1 = 119.36$, $bH_4C_2C_1H_1 = 180.00$, $bH_5C_2C_1H_1 = -bH_6C_2C_1H_1 = 74.50$, $bBrH_4C_2C_1 = 0.00$
(22) $Br + C_2H_4$	$C_1C_2 = 1.3483$, $C_2Br = 2.4677$, $C_1H_1 = C_1H_2 = 1.0829$, $C_2H_3 = C_2H_4 = 1.0830$, $aC_1C_2Br = 93.37$, $aC_2C_1H_1 = aC_2C_1H_2 = 121.33$, $aC_1C_2H_3 = aC_1C_2H_4 = 121.10$, $bH_1C_1C_2Br = -bH_2C_1C_2Br = 87.98$, $bH_3C_2C_1Br = -bH_4C_2C_1Br = 96.62$
(23) $Br + C_2H_2$	$C_1C_2 = 1.2122$, $C_2Br = 2.2777$, $C_1H_1 = 1.0667$, $C_2H_2 = 1.0705$, $aC_1C_2Br = 107.94$, $aC_2C_1H_1 = 169.06$, $aC_1C_2H_2 = 152.46$, $bH_1C_1C_2Br = 0.00$, $bH_2C_2C_1Br = 180.00$
(24) $Br + NH_3$	$NH_1 = 1.4385$, $H_1Br = 1.5568$, $NH_2 = NH_3 = 1.0262$, $aNH_1Br = 152.13$, $aH_1NH_2 = aH_1NH_3 = 110.71$, $bH_2NH_1Br = -bH_3NH_1Br = 59.06$
(25) $Br + SiH_4$	$SiH_1 = 1.8984$, $SiH_2 = SiH_3 = SiH_4 = 1.4792$, $H_1Br = 1.5601$, $aH_1SiH_2 = aH_1SiH_3 = aH_1SiH_4 = 106.09$, $aSiH_1Br = 180.00$, $bH_3SiH_1H_2 = -bH_4SiH_1H_2 = 120.00$
(26) $Br + PH_3$	$PH_1 = 1.5630$, $H_1Br = 1.6768$, $PH_2 = PH_3 = 1.4020$, $aPH_1Br = 168.28$, $aH_1PH_2 = aH_1PH_3 = 95.90$, $bH_2PH_1Br = -bH_3PH_1Br = 47.58$

[a] Bond lengths are in angstroms and bond angles are in degrees.

In order to consider reactivity between a particular combination of halogen and fuel gases, the elementary reactions between the corresponding halogen atom and the fuel molecule may be indispensable. If there is some light or humidity present in the atmosphere, halogen atoms may be produced through decomposition of halogen molecules. The resulting halogen atoms may react with fuel molecules, and the radicals produced there react with halogen molecules to reproduce halogen atoms and maintain the number of active chain carriers. Then, the total number of active radicals may increase monotonously through continuous decomposition of halogen molecules and, eventually, full reaction may occur inside the container of the concerned gas mixture.

On the other hand, the recent progress of ab initio calculation has made it possible to make pretty accurate energetic calculations of various elementary reactions. As an example, quite a number of investigations have been made for silane combustion, and the main reaction route which enables the spontaneous ignition at room temperature has been clarified through extensive use of ab initio calculations of relevant elementary reactions [4–7]. Eventually, the reaction of silyl radical with oxygen molecule has been found to be the key to understand the low temperature silane combustion, of which the activation energy is zero [4]. A series of elementary reactions starting from this reaction has been found to make a chain branching process, yielding more than one active

radicals from one radical of SiH$_3$ [5–7]. A similar investigation has been carried out for phosphine combustion at low temperatures [8]. It has also been of great help to carry out ab initio calculations to obtain the reaction coordinates besides the energetics of relevant molecules and radicals. As a result, it has been found that the barrier to PH$_2$ + O$_2$ reaction is very low and a series of reactions starting from PH$_2$ + O$_2$ makes a chain branching process, which causes spontaneous ignition of phosphine [8].

In the present paper, ab initio energetic calculations will be made using Gaussian-2 theory [9] for various combinations of halogen atoms and fuel molecules. The results of the calculations will be discussed relevant to the auto-reaction nature at room temperature.

2. Results and discussion

The ab initio calculations have been carried out by Gaussian-94 program [10] on a Cray computer or on an IBM computer. The energetic calculations have been made by Gaussian-2 theory [9] for reactions of hydrogen, methane, ethane, ethylene, acetylene, ammonia, silane, dichlorosilane and phosphine molecules against fluorine, chlorine and bromine atoms.

At first, calculations have been carried out to obtain the optimized structures of the concerned molecules by the HF/6-31G* method. The geometry optimizations have also been made by the MP2 = FULL/6-31G* method. The energy values have been obtained based on Gaussian-2 theory following the procedure developed by Curtiss et al. [9]. The zero point energy correction at 298 K has been made based on the HF/6-31G* frequencies multiplied by a factor of 0.893.

For each combination of a halogen atom and a fuel molecule, the calculation has been carried out to seek for a saddle point on the potential surface. The geometrical parameters for the transition states obtained with the MP2 = FULL/6-31G* method are listed in Table 1, where the numbering of atoms is illustrated in Fig. 1. The energy values of the transition states have been obtained by Gaussian-2 theory and are listed together with the values of the MP2 = FULL/6-31G* method in Table 2.

2.1. Reactions between halogen atoms and the molecules of saturated compounds

For the fuel molecules considered in the present study, all the hydrogen atoms in a molecule are equivalent to each other. In the case of saturated compounds, halogen atom approaches one of the hydrogen atoms in a molecule. For each combination of a halogen atom and a fuel molecule, the saddle point has been searched for on the corresponding potential surface. Actually, the saddle point has been found both by the HF/6-31G* and MP2 = FULL/6-31G* methods for every combination of a halogen atom and a fuel molecule treated in the present study.

For all cases treated in the present study, the energy of the saddle point is higher than the energy sum of the original reactants at the level of the HF/6-31G* and MP2 = FULL/6-31G* methods. However, the values of activation energy calculated by using higher levels of ab initio calculation than the HF/6-31G* and MP2 = FULL/6-31G*
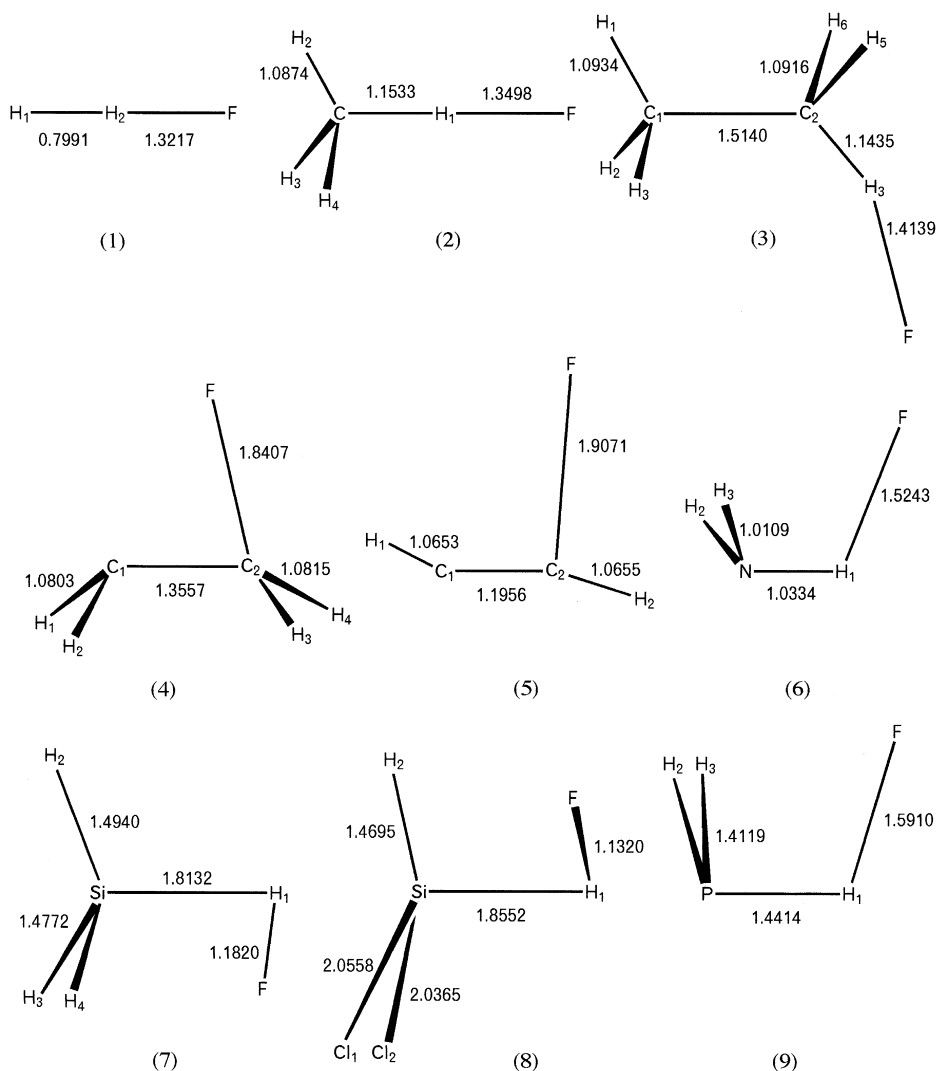
Fig. 1. Transition state structures for the reactions between fluorine atom and fuel molecules by the MP2 = FULL/6-31G* method (see Table 1).

methods are in general much lower than the ones obtained with the latter methods. And for some cases, the G-2 energy value of the potential barrier becomes even lower than that of the original reactants. In these cases, the barrier to the reaction can be considered to be zero. Table 3 summarizes the activation energies calculated from the energies of the transition states listed in Table 2. The numbers in parentheses are the G-2 energies calculated at the optimized geometry by the MP2 = FULL/6-31G* method.

It is remarkable that the activation energies of the reactions of fluorine atom have been found zero whatever the counter part of the reaction. This fact reminds us that

Table 2
Transition state energies (in a.u.) of the reactions between halogen atoms and fuel molecules by Gaussian-2 theory

Reaction	MP2 = FULL/6-31G*	Gaussian-2
(1) $F + H_2$	− 100.61797	− 100.79962
(2) $F + CH_4$	− 139.81406	− 140.04961
(3) $F + C_2H_6$	− 178.98546	− 179.27265
(4) $F + C_2H_4$	− 177.79298	− 178.07196
(5) $F + C_2H_2$	− 176.55790	− 176.83212
(6) $F + NH_3$	− 155.84545	− 156.10781
(7) $F + SiH_4$	− 390.82981	− 391.08342
(8) $F + SiH_2Cl_2$	− 1309.02191	− 1309.49264
(9) $F + PH_3$	− 442.04813	− 442.32288
(10) $Cl + H_2$	− 460.67976	− 460.83136
(11) $Cl + CH_4$	− 499.87044	− 500.07992
(12) $Cl + C_2H_6$	− 539.04603	− 539.30896
(13) $Cl + C_2H_4$	− 537.85902	− 538.10475
(14) $Cl + C_2H_2$	− 536.62630	− 536.86867
(15) $Cl + NH_3$	− 515.89521	− 516.12769
(16) $Cl + SiH_4$	− 750.87300	− 751.10587
(17) $Cl + SiH_2Cl_2$	− 1669.05795	− 1669.51471
(18) $Cl + PH_3$	− 802.11977	− 802.36537
(19) $Br + H_2$	− 2571.09289	− 2573.67132
(20) $Br + CH_4$	− 2610.28146	− 2612.91787
(21) $Br + C_2H_6$	− 2649.45744	− 2652.14674
(22) $Br + C_2H_4$	− 2648.28070	− 2650.95425
(23) $Br + C_2H_2$	− 2647.04703	− 2649.71771
(24) $Br + NH_3$	− 2626.30757	− 2628.96449
(25) $Br + SiH_4$	− 2861.28931	− 2863.94857
(26) $Br + PH_3$	− 2912.54009	− 2915.21427

fluorine is extremely active and reacts immediately with any kind of fuel gas at room temperature [1–3]. It is quite possible that the auto-reaction nature of a fuel gas against fluorine gas is practically determined by the zero activation energy for the reaction between the fuel gas molecule and fluorine atom.

For chlorine atom, the activation energies for the reactions with hydrogen, methane and ammonia are higher than zero while those with ethane, silane, dichlorosilane and phosphine are zero. The activation energies for the former three are 7.29, 4.77, and 4.75 kcal/mol, respectively. As expected, chlorine gas reacts readily with the latter four at room temperature while it does not with the former three [1–3]. In particular, those gases as silane, dichlorosilane, and phosphine are said to react violently with chlorine if they are brought into contact with each other. This is consistent with the well-known fact that the reaction does not in general proceed at a favorable rate at room temperature if the activation energy is higher than 2–3 kcal/mol as well. This is because a small increase of activation energy drastically decreases the reaction rate at room temperature; each increase of 1.0 kcal/mol in the activation energy decreases the reaction rate by a factor of 5.4. Also, the activation energy of the reaction between chlorine atom and

Table 3
Activation energies (in kcal/mol) of the reactions between halogen atoms and fuel molecules by Gaussian-2 theory[a]

(1) $F + H_2$	0.00 (−0.28)
(2) $F + CH_4$	0.00 (−3.70)
(3) $F + C_2H_6$	0.00 (−5.61)
(4) $F + C_2H_4$	0.00 (−14.56)
(5) $F + C_2H_2$	0.00 (−8.52)
(6) $F + NH_3$	0.00 (−10.26)
(7) $F + SiH_4$	0.00 (−19.18)
(8) $F + SiH_2Cl_2$	0.00 (−19.86)
(9) $F + PH_3$	0.00 (−6.93)
(10) $Cl + H_2$	7.29
(11) $Cl + CH_4$	4.77
(12) $Cl + C_2H_6$	0.00 (−0.91)
(13) $Cl + C_2H_4$	0.00 (−7.65)
(14) $Cl + C_2H_2$	0.00 (−3.96)
(15) $Cl + NH_3$	4.75
(16) $Cl + SiH_4$	0.00 (−6.40)
(17) $Cl + SiH_2Cl_2$	0.00 (−6.22)
(18) $Cl + PH_3$	0.00 (−6.10)
(19) $Br + H_2$	16.07
(20) $Br + CH_4$	14.78
(21) $Br + C_2H_6$	9.24
(22) $Br + C_2H_4$	0.00 (−4.86)
(23) $Br + C_2H_2$	0.00 (−0.88)
(24) $Br + NH_3$	15.51
(25) $Br + SiH_4$	0.66
(26) $Br + PH_3$	0.00 (−2.93)

[a] The number in parenthesis is the G-2 energy calculated at the MP2 = FULL/6-31G* geometry.

ethane molecule is zero. As expected, ethane reacts with chlorine at room temperature, though the reaction may not be very violent [1–3]. On the other hand, ammonia is said to react with chlorine at room temperature in spite of the fact that the activation energy of the reaction between chlorine atom and ammonia molecule is much higher than zero. In this case, however, nature of the reaction may be quite different from the cases discussed in the above; hydrogen chloride is produced in some way, which reacts with ammonia with no barrier to the reaction.

The reactivity of bromine atom is very similar to that for chlorine atom. The activation energies for the reactions of bromine atom with hydrogen, methane, ethane, and ammonia are higher than zero; the values are 16.07, 14.78, 9.24 and 15.51 kcal/mol, respectively. Bromine gas may not react readily with these four kinds of gases at room temperature. The activation energy between bromine atom and silane molecule is larger than zero, but the value is only 0.66 kcal/mol and, therefore, the reaction between them may proceed at a favorable rate at room temperature.

In this way, it seems that a negligible value of activation energy of the reaction between a halogen atom and a fuel molecule can be considered indicative of the occurrence of auto-reaction between the corresponding halogen gas and the fuel gas.

2.2. Reactions between halogen atoms and unsaturated compounds

In general, the reaction between a halogen atom and a molecule of an unsaturated compound is an addition reaction. The halogen atom attacks one of the carbon atoms that is involved in an unsaturated bond (see Fig. 1); e.g. the reaction of fluorine atom with ethylene molecule may yield fluoroethyl radical, and the one with acetylene molecule may produce fluorovinyl radical.

The ab initio calculations for unsaturated compounds have been carried out similarly to the saturated compounds, and the energies of the corresponding transition states have been obtained. For any of fluorine, chlorine, and bromine atoms, the activation energies of the reactions with ethylene and acetylene molecules calculated at the level of Gaussian-2 theory have been found zero. Incidentally, the reactions of fluorine, chlorine, and bromine gases with these unsaturated compounds are known to proceed spontaneously [1–3]. Thus, the zero activation energy for these cases is consistent with the auto-reaction nature of these gases with the corresponding halogen gases as well.

2.3. Relevance to the heat of reactions and bond dissociation energies

It is well known that the heat of reaction is a convenient index for a first guess of the reaction hazard of any particular combination of substances. In fact, the hazard of mixing different materials together is often discussed in relevance with the heat of reaction. Three factors have to be taken into account to discuss the relevance of the heat of reaction to the flammability characteristics of gases; i.e. the heat of reaction itself, heat capacity of the reaction products and the limit flame temperature that allows the flame propagation. The ratio of the heat of reaction against the total heat capacity of reaction products may be the quantity that is to be compared with the limit flame

Table 4
Bond dissociation energies (in kcal/mol) of halogen and fuel molecules by Gaussian-2 theory [a]

Molecule	Calculated	Thermo-data
F_2	37.48	37.76[b]
Cl_2	56.58	58.16[b]
Br_2	50.94	46.09[b]
H_2	105.28	104.19[b]
CH_4	105.80	104.80[b]
C_2H_6	102.62	99.5[c]
NH_3	107.91	106.32[b]
SiH_4	92.77	93.93[d]
$SiH_2Cl_2(H)$	93.14	–
$SiH_2Cl_2(Cl)$	111.19	–
PH_3	82.95	80.90[d]

[a] The values at 298 K.
[b] Refs. [11,12].
[c] Ref. [13].
[d] Ref. [14].

temperature for flame propagation, the latter being closely related to the activation energy of the system. Thus, the heat of reaction should be related to the flammability limits rather than to spontaneity of the reaction.

Table 4 contains the values of bond dissociation energies calculated by Gaussian-2 theory together with the literature values [11–14]. The bond dissociation energy is sometimes related to the activation energy. For example, Kerr [15] has modified Polanyi's equation to estimate the activation energy from the bond dissociation energy. For the molecules treated here, however, Kerr's equation does not seem to work well. This is because many of the activation energies treated here are very small or null. If it does, it may work well among such molecules as saturated hydrocarbons. Therefore, it may not be worth relating the auto-reaction property to the bond dissociation energy for molecules like the ones treated in the present study.

3. Conclusion

Ab initio calculations have been carried out by using Gaussian-2 theory for the reactions between various combinations of halogen atoms and fuel molecules, i.e. fluorine, chlorine, and bromine atoms vs. hydrogen, methane, ethane, ethylene, acetylene, ammonia, silane, dichlorosilane and phosphine.

In the case of fluorine or chlorine atom, if the activation energy of reaction with a fuel molecule is zero or close to zero (2–3 kcal/mol or lower), the corresponding halogen and fuel gases react spontaneously with each other at room temperature when they are brought into contact. In particular, inorganic flammable gases such as silane, dichlorosilane and phosphine are extremely reactive and the activation energies of the reactions with halogen atoms are in general zero or close to zero. They are known to immediately react with fluorine and chlorine gases when they are brought into contact with each other. Also, unsaturated hydrocarbons such as ethylene and acetylene are very reactive against halogen gases and immediately react with any of fluorine, chlorine and bromine gases, where the corresponding activation energies are very low as well.

On the other hand, such gases as hydrogen, methane and ammonia do not react immediately with halogen gases other than fluorine at room temperature. The activation energies of the reactions of these gases with chlorine and bromine atoms are of sizable magnitudes. According to the calculation made in the present study, the reactivity of ethane is intermediate between methane and ethylene. It may easily react with chlorine but probably not with bromine.

In conclusion, although there can be some exceptions, the value of activation energy for the reaction between a halogen atom and a fuel molecule seems to be indicative of whether the reaction proceeds spontaneously at room temperature between the corresponding halogen and fuel gases.

References

[1] N.I. Sax, Dangerous Properties of Industrial Materials, 5th edn., Van Nostrand-Reinhold, New York, 1979.

[2] W. Braker, A.L. Mossman, Matheson Gas Data Book, 6th edn., Matheson Gas Products, Secancus, NJ, 1980.

[3] L'Air Liquide, Gas Encyclopedia, Elsevier, 1976.

[4] C.L. Darling, H.B. Schlegel, J. Phys. Chem. 98 (1994) 8910.

[5] Y. Murakami, M. Koshi, H. Matsui, K. Kamiya, H. Umeyama, J. Phys. Chem. 100 (1996) 17501.

[6] S. Kondo, K. Tokuhashi, H. Nagai, A. Takahashi, M. Kaise, M. Sugie, M. Aoyagi, K. Mogi, S. Minamino, J. Phys. Chem. A 101 (1997) 6015.

[7] S. Kondo, K. Tokuhashi, H. Nagai, A. Takahashi, M. Kaise, M. Sugie, M. Aoyagi, S. Minamino, THEOCHEM 469 (1999) 25.

[8] S. Kondo, K. Tokuhashi, A. Takahashi, M. Kaise, M. Sugie, M. Aoyagi, S. Minamino, J. Phys. Chem. A 103 (1999) 8082.

[9] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.

[10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayara, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Gaussian, Pittsburgh, PA, 1995.

[11] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Shumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, J. Phys. Chem. Ref. Data 11 (Suppl. No. 2) (1982).

[12] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, 3rd edn., J. Phys. Chem. Ref. Data 14 (Suppl. No. 1) (1985).

[13] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.

[14] H. Yokokawa, M. Fujishige, S. Ujiie, M. Dokiya, J. Natl. Chem. Lab. 83 (Suppl. No. 1) (1988).

[15] J.A. Kerr, Chem. Rev. 66 (1966) 465.