



Theoretical calculation of heat of formation and heat of combustion for several flammable gases

Shigeo Kondo^{a,*}, Akifumi Takahashi^b, Kazuaki Tokuhashi^b

^a *Research Institute of Innovative Technology for the Earth, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

^b *National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

Received 20 October 2001; received in revised form 5 January 2002; accepted 7 January 2002

Abstract

Heats of formation have been calculated by the Gaussian-2 (G2) and/or G2MP2 method for a number of flammable gases. As a result, it has been found that the calculated heat of formation for compounds containing, such atoms as fluorine and chlorine tends to deviate from the observed values more than calculations for other molecules do. A simple atom additivity correction (AAC) has been found effective to improve the quality of the heat of formation calculation from the G2 and G2MP2 theories for these molecules. The values of heat of formation thus obtained have been used to calculate the heat of combustion and related constants for evaluating the combustion hazard of flammable gases.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gaussian-2; AAC-G2MP2; Heat of formation; Heat of combustion; RF-number

1. Introduction

In order to cope with recent global environmental problems, a number of hydrofluorocarbons (HFCs) have been developed as CFC replacements. In addition, partially fluorinated ethers (HFEs) are considered candidates for new generation CFC replacements. The CFC replacements usually contain hydrogen atoms in the molecule and some of them are flammable. Therefore, the evaluation of flammability hazard is crucial for these compounds.

* Corresponding author. Tel.: +81-298-61-4770; fax: +81-298-61-4770.

E-mail address: s.kondo@aist.go.jp (S. Kondo).

For that purpose, we have recently introduced an index called RF-number, which is defined by the following equation [1].

$$\text{RF} = \frac{FQ}{(1 - F)M} \quad (1)$$

Here, F is a sort of normalized flammable range called F -number, Q the molar heat of combustion, and M the molecular weight. F -number is defined by the following equation [2]:

$$F = 1.0 - \sqrt{\frac{\text{LFL}}{\text{UFL}}} \quad (2)$$

where UFL and LFL are the upper and lower flammability limits, respectively.

RF-number is a number assigned to each flammable gas to represent the combustion hazard of the assigned substance. It has been defined as a product of ignition probability and the possible hazard in case of ignition. In the case of flammable gases, the ignition probability is essentially dependent upon the flammability range in the air. The ignition probability becomes large if the flammable range is wide. However, it should also be noted that the ignition probability becomes large if the lower flammability limit is small because if it is the case the explosive mixture is easily produced at the spot of gas leak. On the other hand, once a certain amount of flammable gas mixture is ignited, the possible hazard is among others dependent upon the amount of heat relieved by the combustion or explosion of the mixture. Therefore, we can adequately evaluate and in particular classify the combustion hazard of materials in terms of RF-number.

Due to the definition of RF-number, the heat of combustion is required to calculate the value of RF-number. Unfortunately, however, the data are very limited. On the other hand, the recent development of computational hardware and software enables accurate estimation of the heat of formation for relatively small molecules. Gaussian-2 (G2) [3] and G2MP2 [4] are typical methods used for such calculations.

However, Berry et al. have found that the calculated values of heat of formation for halogenated compounds are not very good [5]. They say that the heat of formation calculated by these methods exhibit systematic errors up to -50 kJ/mol compared with experimental values and that there is some room to improve the quality of the calculated values by introducing a simplified procedure of bond additivity correction. In this paper, we have applied a similar method to obtain reliable estimates of the heat of formation and heat of combustion to estimate the combustion hazard for a number of flammable gases.

2. Results and discussion

The calculation of enthalpy by G2 [3] and G2MP2 methods [4] has been done by Gaussian 94 program [6] on IBS RS/6000 series computer. The G2 calculation has been carried out for some 30 compounds and G2MP2 calculation for some 70 compounds. The calculated values of enthalpy at 298 K have been converted to heat of formation by the atomization method [7] using the experimental heat of formation of relevant atoms [8]. Table 1 compares

Table 1
G2 and AAC-G2 calculated heat of formation as compared with the observed values (kJ/mol)

Compound	Observed	G2	Observed– calculated	AAC-G2	Observed– calculated
CH ₄	–74.8	–77.4	2.6	–77.4	2.6
C ₂ H ₆	–84.7	–85.5	0.8	–85.5	0.8
C ₂ H ₄	52.3	54.0	–1.7	54.0	–1.7
C ₂ H ₂	226.7	233.9	–7.2	233.9	–7.2
CH ₃ F	–234.0	–243.5	9.5	–234.5	0.5
CH ₃ Cl	–80.8	–85.2	4.4	–83.4	2.6
CH ₂ F ₂	–446.9	–462.8	15.9	–444.7	–2.2
CH ₂ FCl	–261.9	–272.7	10.8	–261.8	–0.1
H ₂ Cl ₂	–92.5	–97.7	5.2	–94.0	1.5
CHF ₃	–688.3	–712.8	24.5	–685.6	–2.7
CHF ₂ Cl	–481.6	497.1	15.5	–477.2	–4.4
CHFC1 ₂	–283.3	–295.1	11.8	–282.4	–0.9
CHCl ₃	–103.1	–107.2	4.0	–101.6	–1.5
CF ₄	–925.0	–955.0	30.0	–918.7	–6.3
CH ₃ CH ₂ F	–261.5	–278.8	17.3	–269.8	8.3
CH ₃ CH ₂ Cl	–112.2	–114.7	2.6	–112.9	0.7
CH ₃ CHF ₂	–478.2	–515.2	37.0	–497.1	18.9
CH ₃ CHCl ₂	–129.4	–141.0	11.6	–137.3	7.9
<i>trans</i> -CH ₂ ClCH ₂ Cl	–129.8	–138.6	8.8	–134.9	5.1
CH ₂ CF ₂	–328.9	–357.9	29.0	–339.7	10.8
<i>trans</i> -CHFCHF	–310.0	–313.8	3.8	–295.7	–14.3
CH ₂ CFCl	–165.4	–173.1	7.7	–162.2	–3.2
CH ₂ CCl ₂	2.4	0.2	2.2	4.0	–1.5
<i>trans</i> -CHClCHCl	6.2	0.8	5.4	4.5	1.7
CHCF	126.0	105.8	20.2	114.9	11.1
CHCCl	213.8	230.4	–16.6	232.2	–18.4
CH ₃ OH	–200.7	–206.0	5.3	–204.2	3.5
CH ₃ CHO	–166.2	–170.3	4.2	–168.6	2.4
CH ₃ COOH	–432.2	–437.5	5.2	–434.0	1.7
HCOOCH ₃	–350.2	–349.0	–1.2	–345.5	–4.7
NH ₃	–46.1	–45.1	–1.0	–49.2	3.1
CH ₃ NH ₂	–23.0	–22.7	–0.3	–26.7	3.8
CH ₃ CN	65.2	76.1	–10.9	72.1	–6.8
Average deviation			10.1		4.9

the G-2 calculated values of heat of formation with the observed values [9,10]. Agreement of the calculated values to the observed ones is in general good. As is seen in Table 1, however, relatively large discrepancies are noted for some compounds and particularly for halogenated compounds, such as CHF₃, CF₄ and CH₃CHF₂.

Recently, Berry et al. have attempted to make a simple correction to the G2 and G2MP2 values of heat of formation [5]. The correction is of the bond additive type. Although, this method is very simple, agreement of the calculated values of heat of formation to the observed ones has been much improved for halogenated compounds. They have only treated methane derivatives, but the same method may be applicable to larger molecules. In the

present study, the correction terms for oxygen and nitrogen atoms have been introduced as well. Although, the correction should essentially be of bond additive nature, we have dealt with the atom additive type correction (AAC); the present method of correcting the heat of enthalpy is given by the following equation:

$$\Delta H_{\text{AAC}} = aN_{\text{N}} + bN_{\text{O}} + cN_{\text{F}} + dN_{\text{Cl}} \quad (3)$$

Here N_{N} , N_{O} , N_{F} and N_{Cl} are the numbers of nitrogen, oxygen, fluorine, and chlorine atoms in the molecule, respectively. The values of parameters, a , b , c and d , have been determined so that the agreement between the observed and calculated values of heat of formation may become best, i.e. the residual value in the least-squares calculation may become minimum.

Table 1 compares the G2 and AAC-G2 calculated values of heat of formation with the observed values. In the least squares calculation to yield the AAC-G2 values, 33 observed values have been used. Introduction of the AAC correction reduced the residual value to one-fourth of the original and reduced the average error from 10.1 to 4.9 kJ/mol. The effect of AAC correction has especially been noted for the halogenated compounds. For example, the discrepancies for CHF_3 , CF_4 and CH_3CHF_2 have reduced from 24.5, 30.0 and 37.0 to -2.7 , -6.3 and 18.9, respectively. As a whole, the agreement has been improved for the nitrogen and oxygen containing compounds as well. The resulting values of parameters a , b , c , and d are shown in Table 2. The value of c is the largest and that of a is next largest, while b and d are small compared to the other two. In other words, the correction for fluorine containing compounds is the largest, that for nitrogen containing compounds is the next and that for oxygen and chlorine containing ones are relatively small.

Similarly, Table 3 shows the result for the G2MP2 method. In this case, 39 observed values in total have been used. Both the calculated values with and without the AAC correction have been compared to the observed values. Introduction of the AAC correction reduced the residual value to one-sixth of the original in this case. The average deviation of the calculated values of heat of formation from the observed ones has been reduced from 13.9 to 5.0 kJ/mol. Although the G2MP2 method is more approximate than the G2 method, it is remarkable that the average deviation of the AAC corrected values of G2MP2 from the observed ones is about the same as that of G2. By the present procedure, the agreement has been improved for the nitrogen and oxygen containing compounds as well, though the effect of the AAC correction is largest for the fluorine compounds. In Table 4, the values of heat of formation calculated by the AAC-G2 and/or AAC-G2MP2 method as well as the ones by G2 and/or G2MP2 method itself are given for a number of additional compounds for which there are no experimental data. The calculations with the G2 method have only done for limited compounds because of the computer resource problem.

Table 2
Coefficients for the AAC of heat of formation

Coefficient	AAC-G2	AAC-G2MP2
a (N)	-4.04	-4.80
b (O)	1.76	5.03
c (F)	9.06	10.69
d (Cl)	1.85	5.92

Table 3
G2MP2 and AAC-G2MP2 calculated heat of formation as compared with the observed values (kJ/mol)

Compound	Observed	G2MP2	Observed– calculated	AAC-G2MP2	Observed– calculated
CH ₄	–74.8	–75.3	0.5	–75.3	0.5
C ₂ H ₆	–84.7	–82.6	–2.1	–82.6	–2.1
C ₂ H ₄	52.3	56.1	–3.8	56.1	–3.8
C ₂ H ₂	226.7	236.1	–9.4	236.1	–9.4
2,2-Dimethyl propane	–167.4	–162.6	–4.8	–162.6	–4.8
CH ₃ F	–234.0	–244.4	10.4	–233.7	–0.3
CH ₃ Cl	–80.8	–87.7	6.9	–81.8	1.0
CH ₂ F ₂	–446.9	–466.0	19.1	–444.6	–2.3
CH ₂ FCl	–261.9	–277.6	15.7	–261.0	–0.9
CH ₂ Cl ₂	–92.5	–104.8	12.3	–92.9	0.5
CHF ₃	–688.3	–717.6	29.3	–685.5	–2.8
CHF ₂ Cl	–481.6	–503.7	22.1	–476.4	–5.2
CHFC1 ₂	–283.3	–303.9	20.6	–281.4	–1.9
CHCl ₃	–103.1	–118.7	15.5	–100.9	–2.2
CF ₄	–925.0	–961.0	36.0	–918.2	–6.8
CH ₃ CH ₂ F	–261.5	–278.6	17.1	–267.9	6.4
CH ₃ CH ₂ Cl	–112.2	–116.3	4.1	–110.4	–1.8
CH ₃ CHF ₂	–478.2	–517.1	38.9	–495.7	17.5
CH ₃ CHCl ₂	–129.4	–147.0	17.6	–135.2	5.8
<i>trans</i> -CH ₂ ClCH ₂ Cl	–129.8	–144.6	14.8	–132.8	3.0
CH ₂ CF ₂	–328.9	–360.2	31.3	–338.8	9.9
<i>trans</i> -CHFCHF	–310.0	–316.7	6.7	–295.4	–14.7
CH ₂ CFCl	–165.4	–177.7	12.3	–161.1	–4.3
CH ₂ CCl ₂	2.4	–6.8	9.2	5.1	–2.6
<i>trans</i> -CHClCHCl	6.2	–6.3	12.4	5.5	0.6
CHCF	126.0	105.3	20.7	116.0	10.0
CHCCl	213.8	228.0	–14.2	233.9	–20.1
CH ₃ CF ₃	–736.4	–773.9	37.5	–741.8	5.4
CH ₃ CCl ₃	–142.3	–167.7	25.4	–150.0	7.7
CH ₃ OH	–200.7	–207.8	7.1	–202.7	2.1
CH ₃ CHO	–166.2	–171.1	5.0	–166.1	–0.1
CH ₃ COOH	–432.2	–440.9	8.7	–430.9	–1.4
HCOOCH ₃	–350.2	–352.9	2.7	–342.9	–7.3
CH ₃ CHOHCH ₂ OH	–421.5	–438.4	16.9	–428.4	6.9
Butylaldehyde	–207.5	–209.7	2.2	–204.7	–2.8
Epichlorohydrin	–107.8	–123.3	15.5	–112.3	4.5
NH ₃	–46.1	–45.6	–0.5	–50.4	4.3
CH ₃ NH ₂	–23.0	–21.8	–1.1	–26.6	3.7
CH ₃ CN	65.2	78.0	–12.8	73.2	–8.0
Average deviation			13.9		5.0

The values of heat of formation have been converted to the heat of combustion according to the usual procedure, i.e. by assuming that F, Cl, and Br atoms contained in the fuel molecules are converted to HF, HCl, and HBr by the combustion reaction as far as there are enough hydrogen atoms, while N atoms in the molecule are converted to N₂ molecules.

Table 4
Predicted values of heat of formation for several combustible gases (kJ/mol)

Compound	G2	AAC-G2	G2MP2	AAC-G2MP2
3-Ethyl-1-butene	–	–	–19.4	–19.4
<i>trans</i> -CH ₂ FCH ₂ F	–456.9	–438.8	–459.5	–438.1
Allyl chloride	2.2	4.0	0.8	6.7
1-Chloropropylene	–8.8	–6.9	–10.0	–4.0
CH ₃ CF ₂ Cl	–	–	–559.5	–532.2
<i>trans</i> -CHF ₂ CHF ₂	–	–	–911.4	–868.7
CH ₃ CFCl ₂	–	–	–357.1	–334.6
CH ₃ CHClCH ₂ Cl	–	–	–181.9	–170.1
1,3-Dichloropropene	–	–	–32.5	–20.6
2,3-Dichloropropene	–	–	–42.6	–30.8
2-Chlorobutene-2	–	–	–51.7	–45.7
CH ₃ CHCHCH ₂ Cl	–	–	–29.2	–23.2
CH ₂ C(CH ₃)CH ₂ Cl	–	–	–34.6	–28.7
2-Chloro-1,3-butadiene	–	–	80.4	86.3
CH ₂ CHCHO	–66.4	–64.7	–66.6	–61.6
Propylene oxide	–98.0	–96.2	–98.2	–93.2
CH ₃ OCF ₃	–	–	–879.6	–842.5
Ethyl formate	–	–	–405.4	–395.3
CH ₂ ClCOOCH ₃	–	–	–433.5	–417.6
(CH ₃) ₂ CHCHO	–	–	–214.6	–209.6
CH ₃ OCH ₂ OCH ₃	–	–	–343.9	–333.8
Methyl vinyl ketone	–	–	–110.4	–105.4
Crotonyl alcohol	–	–	–151.9	–146.9
CH ₂ CH(CH ₂) ₂ OH	–	–	–147.3	–142.3
Vinyl ethyl ether	–	–	–133.8	–128.8
1,2-Butylene oxide	–	–	–114.7	–109.7
2,3-Butylene oxide	–	–	–138.1	–133.1
Divinyl ether	–	–	1.8	6.8
Allylamine	60.2	56.2	62.6	57.8
C ₃ H ₅ CN	–	–	160.0	155.2

Here, the heats of combustion have been obtained on the basis of water vapor production. The result is given in Table 5, where M is molecular weight, LFL the lower flammability limit, UFL the upper flammability limit, C_{st} the stoichiometric concentration, ΔH_c the heat of combustion, F the F -number, and RF the RF-number.

In order to evaluate the combustion hazard of gases, the use of RF-number is convenient, the value of which can be calculated by using Eq. (1) from the data of heat of combustion together with the data of flammability limits and are listed in the eighth column of Table 5, where the flammability limits data (LFL and UFL) are from the literature [11]. The RF-number values of saturated hydrocarbons, such as methane and ethane range, for example, from 30 to 60 kJ/g. It is noted that the RF-number values of ethylene and acetylene are larger than 100. On the contrary, the RF-number values of heavily halogenated methanes and ethanes are very small, e.g. <10 or so.

Table 5
Flammability characteristics of molecules treated in the present study

Compound	<i>M</i> (g/mol)	LFL (vol.%)	UFL (vol.%)	<i>C</i> _{st} (vol.%)	ΔH_c (kJ/mol)	<i>F</i>	RF (kJ/g)
CH ₄	16.0	5.0	15.0	9.5	802	0.42	36.6
C ₂ H ₆	30.1	3.0	12.5	5.7	1428	0.51	49.4
C ₂ H ₄	28.1	2.7	36.0	6.5	1323	0.73	125.0
C ₂ H ₂	26.0	2.5	100.0	7.7	1256	0.84	256.8
2,2-Dimethyl propane	72.2	1.4	7.5	2.6	3251	0.57	59.2
3-Methyl-1-butene	70.1	1.5	9.1	2.7	3157	0.59	65.9
CH ₃ F	34.0	6.8	20.3	12.3	672	0.42	14.4
CH ₃ Cl	50.5	8.1	17.4	12.3	647	0.32	6.0
CH ₂ F ₂	52.0	13.3	29.3	17.3	489	0.33	4.6
CH ₂ FCl	68.5	14.4	26.5	17.3	495	0.26	2.6
CH ₂ Cl ₂	84.9	14.0	22.0	17.3	486	0.20	1.5
CHF ₃	70.0	13.3	29.3	29.5	242	0.33	1.7
CHF ₂ Cl	86.5	13.3	29.3	21.8	316	0.33	1.8
CHFCl ₂	102.9	13.3	29.3	17.3	381	0.33	1.8
CHCl ₃	119.4	13.3	29.3	17.3	383	0.33	1.6
CF ₄	88.0	13.3	29.3	100.0	0	0.33	0.0
CH ₃ CH ₂ F	48.1	3.8	15.4	6.5	1280	0.50	7.0
CH ₃ CH ₂ Cl	64.5	3.8	15.4	6.5	1251	0.50	19.6
CH ₃ CHF ₂	66.1	4.8	17.3	7.7	1093	0.47	14.9
CH ₃ CHCl ₂	99.0	4.8	17.3	7.7	1084	0.47	9.8
<i>trans</i> -CH ₂ ClCH ₂ Cl	99.0	6.2	16.0	7.7	1084	0.38	6.6
CH ₂ CF ₂	64.0	5.5	21.3	9.5	1000	0.49	15.1
<i>trans</i> -CHFCHF	64.0	5.5	21.3	9.5	1019	0.49	15.4
CH ₂ CFCI	80.5	2.6	21.7	9.5	985	0.65	23.1
CH ₂ CCl ₂	96.9	6.5	15.5	9.5	974	0.35	5.5
<i>trans</i> -CHClCHCl	96.9	5.6	12.8	9.5	978	0.34	5.2
CHCF	44.0	2.5	100.0	9.5	1184	0.84	143.2
CHCCl	60.5	2.5	100.0	9.5	1093	0.84	96.2
CH ₃ CF ₃	84.0	7.0	19.0	9.5	864	0.39	6.7
CH ₃ CCl ₃	133.4	7.5	12.5	9.5	922	0.23	2.0
Epichlorohydrin	92.5	3.8	21.0	5.7	1649	0.57	24.1
<i>trans</i> -CH ₂ FCH ₂ F	66.1	4.8	17.3	7.7	1132	0.47	15.4
Allyl chloride	76.5	2.9	11.1	5.0	1760	0.49	22.0
1-Chloropropylene	76.5	4.5	16.0	5.0	1750	0.47	20.3
CH ₃ CF ₂ Cl	100.5	7.8	16.8	9.5	889	0.32	4.1
<i>trans</i> -CHF ₂ CHF ₂	102.0	6.2	22.6	12.3	726	0.48	6.5
CH ₃ CFCI ₂	117.0	9.0	15.4	9.5	908	0.24	2.4
CH ₃ CHClCH ₂ Cl	113.0	3.4	14.5	5.0	1679	0.52	15.8
1,3-Dichloropropene	111.0	5.3	14.5	5.7	1586	0.40	9.4
2,3-Dichloropropene	111.0	2.6	7.8	5.7	1576	0.42	10.4
2-Chlorobutene-2	90.6	2.3	9.3	3.7	2346	0.50	26.2
CH ₃ CHCHCH ₂ Cl	90.6	4.2	19.0	3.7	2369	0.53	29.5
CH ₂ C(CH ₃)CH ₂ Cl	90.6	3.2	8.1	3.7	2363	0.37	15.4
2-Chloro-1,3-butadiene	88.5	4.0	20.0	4.0	2236	0.55	31.2
CH ₃ OH	32.0	6.0	36.0	12.3	676	0.59	30.6
CH ₃ CHO	44.1	4.0	36.0	7.7	1104	0.67	50.1
CH ₃ COOH	60.1	4.0	19.9	9.5	838	0.55	17.2
HCOOCH ₃	60.1	4.5	23.0	9.5	920	0.56	19.3
CH ₃ CHOHCH ₂ OH	76.1	2.6	12.5	5.0	1726	0.54	27.1

Table 5 (Continued)

Compound	<i>M</i> (g/mol)	LFL (vol.%)	UFL (vol.%)	<i>C</i> _{st} (vol.%)	ΔH_c (kJ/mol)	<i>F</i>	RF (kJ/g)
Butylaldehyde	72.1	1.9	12.5	3.7	2334	0.61	50.7
CH ₂ CHCHO	56.1	2.8	31.0	5.7	1599	0.70	66.4
Propylene oxide	58.1	2.3	36.0	5.0	1810	0.75	92.1
Ethyl formate	74.1	2.8	16.0	5.7	1510	0.58	28.4
(CH ₃) ₂ CHCHO	72.1	1.6	10.6	3.7	2332	0.61	50.9
CH ₃ OCH ₂ OCH ₃	76.1	2.2	13.8	5.0	1814	0.60	35.9
Methyl vinyl ketone	70.1	2.1	15.6	4.0	2194	0.63	54.0
Crotonyl alcohol	72.1	4.2	35.3	3.7	2394	0.66	63.1
CH ₂ CH(CH ₂) ₂ OH	72.1	4.7	34.0	3.7	2399	0.63	56.2
Vinyl ethyl ether	72.1	1.7	28.0	3.7	2413	0.75	102.3
1,2-Butylene oxide	72.1	1.7	19.0	3.7	2432	0.70	79.0
2,3-Butylene oxide	72.1	1.5	18.3	3.7	2408	0.71	83.3
Divinyl ether	70.1	1.7	27.0	4.0	2306	0.75	98.2
CH ₃ OCF ₃	100.0	10.5	21.5	12.3	758	0.30	3.3
CH ₂ ClCOOCH ₃	108.5	7.5	18.5	6.5	1339	0.36	7.0
NH ₃	17.0	15.0	28.0	21.8	317	0.27	6.8
CH ₃ NH ₂	31.1	4.9	20.7	8.5	975	0.51	33.1
CH ₃ CN	41.1	3.0	16.0	7.1	1215	0.57	38.8
Allylamine	57.1	2.2	22.0	4.2	2083	0.68	78.9
C ₃ H ₅ CN	67.1	2.0	6.8	3.8	2334	0.46	29.4

3. Conclusion

It has been found that the quality of G2MP2 as well as G2 calculated values of heat of formation and heat of combustion are considerably improved by use of a simplified atom additivity correction method. With the present method, the value of heat of combustion can be predicted with uncertainty <10% for moderate size molecules, which is accurate enough to be used to classify the combustion hazard of flammables. The values of heat of combustion have been obtained by the present method of AAC-G2MP2 for a number of molecules for which the experimental data are not available.

Acknowledgements

The present study has been performed with the support of the New Energy and Industrial Technology Development Organization.

References

- [1] S. Kondo, K. Tokuhashi, A. Takahashi, A. Sekiya, Assessment of combustion hazard of flammable gases by using RF-number, in: Proceedings of the 31st Symposium on Safety Engineering, Japan, 2001, p. 325.
- [2] S. Kondo, Y. Urano, K. Tokuhashi, A. Takahashi, K. Tanaka, Prediction of flammability of gases by using *F*-number analysis, *J. Hazard. Mater.* 2605 (2001) 1–16.

- [3] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, *J. Chem. Phys.* 94 (1991) 7221.
- [4] L.A. Curtiss, K. Raghavachari, J.A. Pople, *J. Chem. Phys.* 98 (1993) 1293.
- [5] R.J. Berry, D.R.F. Burgess Jr., M.R. Nyden, M.R. Zachariah, C.F. Melius, M. Schwartz, *J. Phys. Chem.* 100 (1996) 7405.
- [6] 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 Inc., Pittsburgh, PA, 1995.
- [7] A. Nicolaides, A. Rauk, M.N. Glukhovtsev, L. Radom, *J. Phys. Chem.* 100 (1996) 17460.
- [8] CODATA, CODATA recommended key values for thermodynamics 1977, *J. Chem. Thermodyn.* 10 (1978) 903.
- [9] 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 (2) (1982).
- [10] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, 3rd Edition, *J. Phys. Chem. Ref. Data* 14 (1) (1985).
- [11] NFPA, Fire hazard properties of flammable liquids, gases, and volatile solids, NFPA 325M, 1984.