

文章编号: 1006-9941 (2016)09-0838-04

Energies of Combustion and Specific Heat Capacities of Diaminofurazan, Dinitrofurazan and Diaminoazofurazan

LI Yan-feng¹, ZHAI Lian-jie², XU Kang-zhen¹, SONG Ji-rong¹, ZHAO Feng-qi²

(1. School of Chemical Engineering, Northwest University, Xi'an 710069, China; 2. Xi'an Modern Chemistry Research Institute, Xi'an 710065, China)

Abstract: Energies of combustion and specific heat capacities of diaminofurazan (DAF), dinitrofurazan (DNF) and diaminoazofurazan (DAAzF) were determined. Energies of combustion for the three compounds are (-13043 ± 119) , (-6863 ± 37) J · g⁻¹ and (-12661 ± 54) J · g⁻¹, respectively. The corresponding standard molar enthalpies of formation ($\Delta_f H_m^\ominus$) were obtained with the different combustion products. The values of specific heat capacities for the three compounds are (140.8 ± 0.1) , (236.8 ± 0.2) , (216.9 ± 0.2) J · mol⁻¹ · K⁻¹, respectively. Energy of combustion tends to rise with the decrease of oxygen content in molecule (DAF > DAAzF > DNF). Amino group contributes to increase energy of combustion, but nitro group has the opposite effect. As for the specific heat capacity, the change rule is opposite to energy of combustion.

Key words: furazan; energy of combustion; enthalpy of formation; Specific heat capacity

CLC number: TJ55; O642

Document code: A

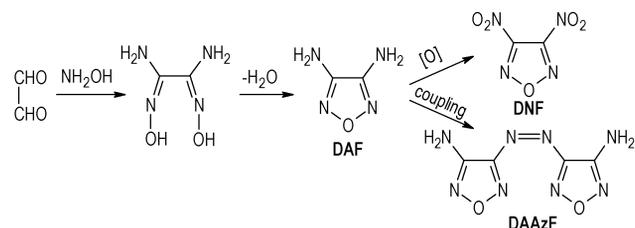
DOI: 10.11943/j.issn.1006-9941.2016.09.003

1 Introduction

As one of the most simple furazan ring compounds, 3,4-diaminofurazan (DAF) features good thermal stability and big density, which make it efficient structural units in the development of high-energy-density materials (HEDMs)^[1-5]. DAF has been an important precursor to a series of furazan-based energetic materials^[6-10], 3,4-dinitrofurazan (DNF), 4,4-dimino-3,3-azofurazan (DAAzF) are two relatively simple derivatives of DAF, and their relationship are shown in Scheme 1. DNF was firstly reported at 1994^[11], having a crystal density of 1.62 g · ml⁻¹, a melting point of 15.8 °C and a boiling point of 168.8 °C. DNF is a high energy explosive and has been exploited the high reactivity of the nitro-groups to nucleophile in the synthesis of a large number of energetic derivatives. DAAzF is another special rich-nitrogen insensitive energetic material for its big positive enthalpy of formation^[12]. Many studies showed that the three furazan compounds have excellent properties and good application prospect^[13-14].

Energy of combustion and specific heat capacity are two important thermodynamic data and characteristic quantities closely related to energy and structure of material. We researched energies of combustion and specific heat capacities of the three furazan ring compounds to enrich thermochemical

database and provide theoretical basis for further application. Meanwhile, the change rule of structure-property for the three compounds was also discussed.



Scheme 1 Relationship of DAF, DNF and DAAzF

2 Experimental

2.1 Samples

DAF, DNF and DAAzF were synthesized by our research group in Xi'an Modern Chemistry Research Institute. Their purities are more than 99.5% (HPLC). DAF and DAAzF are solid, and DNF is liquid.

2.2 Energy of Combustion

Energy of combustion was determined with an IKA C5000 oxygen-bomb calorimeter (German) in adiabatic pattern. The calorimeter was calibrated with the standard substance benzoic acid having a purity of 99.99%, and each sample was tested with 6 times, The mean value (-26504 ± 147) J · g⁻¹^[15] is very close to the standard value as (-26434 ± 3) J · g⁻¹ ($T = 298.15$ K)^[16], indicating that the measuring system is accurate and reliable. The uncertainty can be obtained by equation $U_c = ku$, where u is the standard uncertainty (the standard de-

Received Date: 2016-03-30; **Revised Date:** 2016-05-11

Biography: LI Yan-feng (1991-), male, graduate, research fields: energetic materials. e-mail: 1107404977@qq.com

Corresponding Author: XU Kang-zhen (1976-), male, professor, research field: the synthesis and properties of new energetic materials. e-mail: xukz@nwu.edu.cn

viation of mean) the coverage factor k is 2, and level of confidence is 0.95.

2.3 Specific Heat Capacity

Specific heat capacity was measured using a Micro-DSC III apparatus (SETARAM, France), with the operating temperature range of 283–333 K, temperature accuracy of 10^{-4} K, heat flow accuracy of 10^{-4} mW, and heating rate of $0.15 \text{ K} \cdot \text{min}^{-1}$. The sample mass used for calorimetric measurement was about 200 mg. The reliability of enthalpy measurement was ensured by determinations of the enthalpy of dissolution of KCl (cr) in deionized water at 298.15 K. The result was $(17.27 \pm 0.07) \text{ kJ} \cdot \text{mol}^{-1}$, which was very close to the literature value as $(17.24 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$ [17]. The equation of specific heat capacity for standard calcined $\alpha\text{-Al}_2\text{O}_3$ obtained was $c_p(\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) = 0.184 + 1.997 \times 10^{-3} T$ ($283 \text{ K} < T < 353 \text{ K}$), and the standard molar heat capacity is $79.44 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (298.15 K), which is consistent with the literature value of $79.02 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ [18]. The results indicate that calorimetric equipment is reliable and accurate.

3 Results and Discussion

3.1 Energy of Combustion

Each sample was tested with 6 times, and the results are listed in Table 1. The constant-volume energies of combustion

Table 1 Determination results for the energies of combustion of the samples

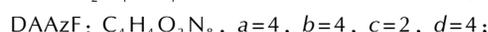
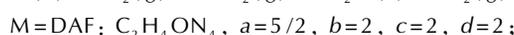
sample	No.	m/g	$\Delta T/\text{K}$	$\Delta_c U/\text{J} \cdot \text{g}^{-1}$
DAF	1	0.15733	0.1983	12954
	2	0.15768	0.2006	13084
	3	0.15719	0.1984	12973
	4	0.15747	0.1997	13040
	5	0.15724	0.1974	12899
	6	0.15733	0.2002	13308
	mean			13043±119
DNF	1	0.14900	0.1045	6860
	2	0.14650	0.1026	6835
	3	0.14330	0.1001	6797
	4	0.14400	0.1018	6893
	5	0.14250	0.0999	6930
	6	0.14367	0.1012	6863
	mean			6863±37
DAAzF	1	0.14390	0.1776	12652
	2	0.14426	0.1791	12745
	3	0.14324	0.1757	12576
	4	0.14366	0.1766	12610
	5	0.14389	0.1774	12652
	6	0.10364	0.1317	12728
	mean			12661±54

Note: m is the mass of the sample; ΔT is the temperature rising; $\Delta_c U$ is the energy of combustion.

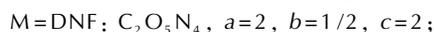
for DAF, DNF and DAAzF are (-13043 ± 119) , (-6863 ± 37) , $(-12661 \pm 54) \text{ J} \cdot \text{g}^{-1}$, respectively. The energy of combustion tends to rise with the decrease of oxygen content in molecule, $\text{DAF} (15.99\%) > \text{DAAzF} (16.31\%) > \text{DNF} (49.98\%)$. DAF and DAAzF exhibit greater energy of combustion than DNF, indicating that amino group is an excellent burning group and markedly increase energy of combustion, but nitro group has the opposite influence. Due to the same number of amino group and the approximate nitrogen content (oxygen content), the difference of energy of combustion for DAF and DAAzF is small.

3.2 Enthalpy of Formation

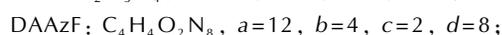
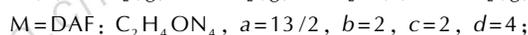
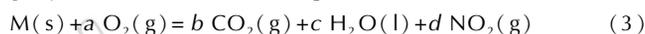
The standard molar enthalpy of combustion ($\Delta_c H_m^\ominus$) was referred to the energy of combustion change of the following idealized reaction equation (1) at $T = 298.15 \text{ K}$ and $p^\ominus = 101.325 \text{ kPa}$ [19].



Herein, it is necessary to illustrate that DNF is an oxygen-rich compound, whose oxygen content reaches 49.98%. It doesn't need extra oxygen in combustion process according to equation (1). In order to obtain the standard molar enthalpy of combustion for DNF, another idealized reaction equation (2) was adopted.



Meanwhile, in consideration of the rich nitro group in these compounds, idealized reaction equation (3) was employed. In the following reaction, NO_2 was considered as the gas product instead of usual N_2 for thermochemical calculation.



The standard molar enthalpy of combustion ($\Delta_c H_m^\ominus$) can be obtained in accordance with equations (4) and (5) from the constant-volume state to the constant-pressure state. The calculated results are listed in Table 2.

$$\Delta_c H_m^\ominus = \Delta_c U_m + \Delta nRT \quad (4)$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \quad (5)$$

where $\sum n_i$ was the total molar amount of gases in products or reactants.

The standard molar enthalpy of formation ($\Delta_f H_m^\ominus$) of the compound can be calculated by Hess's law[19], according to the above thermochemical equations. Taking DAF for instance, the standard molar enthalpy of formation is:

$$\Delta_f H_m^\ominus(\text{DAF, s}) = 2\Delta_f H_m^\ominus(\text{CO}_2, \text{g}) + 2\Delta_f H_m^\ominus(\text{H}_2\text{O, l}) - \Delta_c H_m^\ominus(\text{DAF, s}) \quad (6)$$

where the standard molar enthalpies of formation for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ recommended by CODATA, $\Delta_f H_m^\ominus(\text{CO}_2, \text{g}) = (-393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) = (-285.83 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\ominus(\text{NO}_2, \text{g}) = 33.18 \text{ kJ} \cdot \text{mol}^{-1}$, were used to calculate the values of $\Delta_f H_m^\ominus$ ^[20–21]. The standard molar enthalpies of formation for the three compounds can be calculated and are listed in Table 2.

If N_2 was considered as gas product, DAF has negative enthalpy of formation as $(-57.1 \pm 11.9) \text{ kJ} \cdot \text{mol}^{-1}$, while DNF and DAAzF have positive enthalpy of formation as

$(295.3 \pm 6.0) \text{ kJ} \cdot \text{mol}^{-1}$ and $(327.8 \pm 10.5) \text{ kJ} \cdot \text{mol}^{-1}$. Compared with amino group, nitro group has a greater effect on positive enthalpy of formation. Diazotization structure also contributes to positive enthalpy of formation. Moreover, if NO_2 was considered as gas product, the value of enthalpy of formation of DAF is in close proximity to the literature value as $89.99 \text{ kJ} \cdot \text{mol}^{-1}$ ^[22], which indicates that considering NO_2 as gas product is feasible. Enthalpies of formation for DAF, DNF and DAAzF are (80.6 ± 11.9) , $(437.9 \pm 6.0) \text{ kJ} \cdot \text{mol}^{-1}$ and $(603.1 \pm 10.5) \text{ kJ} \cdot \text{mol}^{-1}$ respectively, and the change rule is consistent with the above.

Table 2 The thermodynamic values for the three furazan compounds at 298.15 K

sample	M / $\text{g} \cdot \text{mol}^{-1}$	$-\Delta_c U_m$ / $\text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_m^{\ominus a}$ / $\text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_m^{\ominus b}$ / $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_m^{\ominus a}$ / $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_m^{\ominus b}$ / $\text{kJ} \cdot \text{mol}^{-1}$
DAF	100.08	1305.3 ± 11.9	1301.6 ± 11.9	1306.6 ± 11.9	-57.1 ± 11.9	80.6 ± 11.9
DNF	160.05	1098.4 ± 6.0	1087.3 ± 6.0	1092.3 ± 6.0	300.3 ± 6.0	437.9 ± 6.0
DAAzF	196.13	2483.1 ± 10.5	2473.5 ± 10.5	2483.1 ± 10.5	327.8 ± 10.5	603.1 ± 10.5

Note: M is the molecular mass; $\Delta_c U_m$ is the constant-volume molar energy of combustion; $\Delta_c H_m^{\ominus a}$ is the standard molar enthalpy of combustion (N_2 as gas product); $\Delta_c H_m^{\ominus b}$ is the standard molar enthalpy of combustion (NO_2 as gas product); $\Delta_f H_m^{\ominus a}$ is the standard molar enthalpy of formation (N_2 as gas product); $\Delta_f H_m^{\ominus b}$ is the standard molar enthalpy of formation (NO_2 as gas product).

3.3 Specific Heat Capacity

The continuous specific heat capacities of DAF, DNF and DAAzF were measured successively. Taking DAAzF as example, the measuring results are shown in Fig. 1. The fitted specific heat capacity equations for the three compounds are listed in Table 3, according to the automatic data processing software of Micro-DSC III apparatus. Relevant specific heat capacities and standard molar heat capacities ($c_{p,m}^\ominus$) of the three compounds at 298.15 K are also listed in Table 3. Specific heat capacities for DAF and DAAzF present linear relationship with temperature in the determining temperature range, but specific heat capacities of DNF presents obvious quadratic relationship with temperature. The specific heat capacities for DAF, DNF and DAAzF at 298.15 K are (1.4067 ± 0.0012) , (1.4797 ± 0.0015) , $(1.1058 \pm 0.0010) \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, respectively. The specific heat capacity of the three compounds decreases in the order of $\text{DNF} > \text{DAF} > \text{DAAzF}$. Nitro group makes a greater contribution to specific heat capacity than amino group, which is opposite to the change tendency

of energy of combustion ($\text{J} \cdot \text{g}^{-1}$). The specific heat capacity of DAF is larger than that of DAAzF, indicating that diazotization structure may decrease the specific heat capacity of compound, but the values of DAF and DAAzF are still close to each other, which is consistent with the result of energy of combustion.

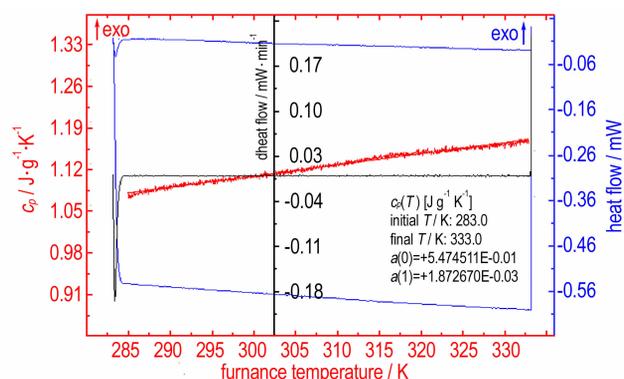


Fig. 1 Determination result of the continuous specific heat capacity of DAAzF

Table 3 Determination results of continuous specific heat capacity at 298.15 K

sample	$E_q / \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ (283–333 K)	r^2	$c_{p,m} / \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ (298.15 K)	$c_{p,m}^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (298.15 K)
DAF	$0.3373 + 3.5868 \times 10^{-3} T$	0.9980	1.4067 ± 0.0012	140.8 ± 0.1
DNF	$-6.7135 + 5.2418 \times 10^{-2} T - 8.3642 \times 10^{-5} T^2$	0.9882	1.4797 ± 0.0015	236.8 ± 0.2
DAAzF	$0.5475 + 1.8727 \times 10^{-3} T$	0.9929	1.1058 ± 0.0010	216.9 ± 0.2

Note: E_q is the specific heat capacity equation; r^2 is the correlation coefficient; $c_{p,m}$ is the specific heat capacity; $c_{p,m}^\ominus$ is the standard molar heat capacity.

4 Conclusions

(1) Energies of combustion of DAF, DNF and DAAzF were determined as (-13043 ± 119) , (-6863 ± 37) , (-12661 ± 54) $\text{J} \cdot \text{g}^{-1}$, respectively. The energy of combustion tends to rise with the decrease of oxygen content in molecule. Amino group contributes to increase energy of combustion, but nitro group has the opposite effect. The corresponding standard molar enthalpies of formation ($\Delta_f H_m^\ominus$) are (-57.1 ± 11.9) , (295.3 ± 6.0) , (327.8 ± 10.5) $\text{kJ} \cdot \text{mol}^{-1}$ with N_2 as gas product. When the gas product is NO_2 , the values of $\Delta_f H_m^\ominus$ are (80.6 ± 11.9) , (437.9 ± 6.0) , (603.1 ± 10.5) $\text{kJ} \cdot \text{mol}^{-1}$, respectively.

(2) The standard molar heat capacities ($c_{p,m}^\ominus$) of the three compounds are (140.8 ± 0.1) , (236.8 ± 0.2) , (216.9 ± 0.2) $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. As for the specific heat capacity, the change rule is opposite to energy of combustion. In addition, diazotization has a faintly negative effect on energy of combustion and specific heat capacity.

References:

- [1] LI Zhan-xiong, TANG Song-qing, OU Yu-xiang, et al. Synthesis status of furazano energetic Derivatives [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2002, 10(2): 59–65.
- [2] Talawar M B, Sivabalan R, Senthilkumar N, et al. Synthesis, characterization and thermal studies on furazan- and tetrazine-based high energy materials [J]. *Journal of Hazardous Materials*, 2004, 113(1–3): 1125.
- [3] GE Zhong-xue, WANG Xi-jie, JIANG Jun, et al. Synthesis of 3, 4-dinitrofurazan [J]. *Chinese Journal of Synthetic Chemistry*, 2008, 116(3): 260–263.
- [4] Veauthier J M, Chavez D E, Tappan B C, et al. Synthesis and characterization of furazan energetics ADAAF and DOATF [J]. *Journal of Energetic Materials*, 2010, 28(3): 229–249.
- [5] Chavez D E, Parrish D A, Leonard P. The synthesis and characterization of a new furazan heterocyclic System [J]. *Synlett*, 2012, 23(14): 2126–2128.
- [6] Sheremetev A B, Kulgina V O, Aleksandrova N S, et al. Dinitro trifurazans with oxy, azo, and azoxy bridges [J]. *Propellants, Explosives, Pyrotechnics*, 1998, 23(3): 142–149.
- [7] Chavez D, Hill S, Hiskey M. Preparation and explosive properties of azo- and azoxy-furazans [J]. *Journal of Energetic Materials*, 2000, 18(2–3): 219–236.
- [8] GE Zhong-xue, LAI Wei-peng, LIAN Peng, et al. Predicting on the detonation performances of poly-furazans with oxy bridges [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2008, 16(3): 280–284.
- [9] ZHANG Yu, WANG Bo-zhou, XU Kang-zhen, et al. Synthesis and characteristics of bis(nitrofurazano) furazan (BNFF), an insensitive material with high energy-density [J]. *Propellants, Explosives, Pyrotechnics*, 2014, 39(6): 809–814.
- [10] ZHAI Lian-jie, WANG Bo-zhou, HUO Huan, et al. Synthesis, crystal structure and thermal behavior of 3, 4-Bis(3-nitrofurazan-4-oxy) furazan [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2015, 23(1): 18–22.
- [11] Novikova T S, Melnikova T M, Kharitonova O V, et al. An effective method for the oxidation of aminofurazans to nitrofurazans [J]. *Mendeleev Commun.* 1994, 4(4): 138–140.
- [12] LI Yu-bin, HUANG Hui, LI Jin-shan, et al. HMX based low sensitive high explosives containing DAAzF [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2008, 16(3): 244–246.
- [13] Pagoria P F. A review of energy materials synthesis [J]. *Thermo-chimica Acta*, 2002, 384(1): 187–204.
- [14] Sikder A K, Sikder N. A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications [J]. *Journal of Hazardous Materials*, 2004, 112(1–2): 1–15.
- [15] SUN Qian, LI Yan-feng, XU Kang-zhen, et al. Crystal structure and enthalpy of combustion of AEFOX-7 [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2015, 23(12): 1235–1239.
- [16] Certificate of Analysis Standard Reference Material 39j Benzoic Acid Calorimetric Standard, NBS, Washington D C, 1995.
- [17] Marthada V K. The enthalpy of solution of SRM 1655 (KCl) in H_2O [J]. *Journal of Research of the National Bureau of Standards*, 1980, 85(6): 467–471.
- [18] Ditmars D A, Ishihara S, Chang S S. Enthalpy and heat-capacity standard reference material: synthetic sapphire ($(\delta)\text{-Al}_2\text{O}_3$) from 10 to 2250 K [J]. *Journal of Research of the National Bureau of Standards*, 1982, 87(2): 159–163.
- [19] Atkins P, Paula J D. *Atkins' Physical Chemistry (7th)* [M]. Beijing: High Education Press, 2006.
- [20] Cox J D. CODATA recommended key values for thermodynamics, 1977 Report of the CODATA Task Group on key values for thermodynamics [J]. *Journal of Chemical Thermodynamics*, 1978, 10(10): 903–906.
- [21] HU Rong-zu, ZHAO Feng-qi, GAO Hong-xu, et al. Fundamentals and application of calorimetry [M]. Beijing: Science Press, 2011.
- [22] TIAN De-yu, ZHAO Feng-qi, LIU Jian-hong. *Handbook of Energetic Materials and the Related Compounds* [M]. Beijing: National Defense Industry Press, 2011.

DAF、DNF 和 DAAzF 的燃烧能和比热容研究

李彦峰¹, 翟连杰², 徐抗震¹, 宋纪蓉¹, 赵凤起²

(1. 西北大学化工学院, 陕西 西安 710069; 2. 西安近代化学研究所, 陕西 西安 710065)

摘要: 测得了二氨基呋咱 (DAF), 二硝基呋咱 (DNF) 及二氨基偶氮呋咱 (DAAzF) 的燃烧能和比热容。三种化合物的燃烧能分别为 (-13043 ± 119) , (-6863 ± 37) 和 (12661 ± 54) $\text{J} \cdot \text{g}^{-1}$, 同时, 计算得到了基于不同燃烧产物的标准摩尔生成焓 ($\Delta_f H_m^\ominus$)。三种化合物 298.15 K 时的标准摩尔热容分别为 (140.8 ± 0.1) , (236.8 ± 0.2) , (216.9 ± 0.2) $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ 。燃烧能随着分子中氧含量的增加而减少 (DAF > DAAzF > DNF)。氨基基团有助于提高燃烧能, 硝基则有负作用。对于比热容而言, 三种化合物的变化规律与燃烧能相反。

关键词: 呋咱; 燃烧能; 生成焓; 比热容

中图分类号: TJ55; O642

文献标志码: A

DOI: 10.11943/j.issn.1006-9941.2016.09.003