Synthesis, crystal structure, sensitivity, and effect on thermal decomposition of ammonium perchlorate: an energetic compound Cu(HATZ)(PDA)(H$_2$O)

Qi Yang [a] , Sanping Chen [a] , Gang Xie [a] & Shengli Gao [a]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education , College of Chemistry and Materials Science, Northwest University , Xi'an , Shaanxi 710069 , China
Accepted author version posted online: 07 Jun 2012.Published online: 14 Jun 2012.

PLEASE SCROLL DOWN FOR ARTICLE

Synthesis, crystal structure, sensitivity, and effect on thermal decomposition of ammonium perchlorate: an energetic compound Cu(HATZ)(PDA)(H₂O)

QI YANG, SANPING CHEN*, GANG XIE and SHENGLI GAO

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, China

An energetic coordination compound, Cu(HATZ)(PDA)(H$_2$O) (HATZ = 5-aminotetrazole, H$_2$PDA = pyridine-2,6-dicarboxylic acid), has been synsized and structurally characterized by single crystal X-ray diffraction. Copper(II) was coordinated by two oxygen atoms and nitrogen from PDA, one ring nitrogen of ATZ and one water to form a five-coordinate, distorted square-pyramidal structure. 3-D supramolecular architecture was formed by hydrogen bonding. Thermal decomposition of the compound was examined by DSC and TG-DTG analyses. The kinetic parameters of the first exothermic process of the compound were studied by Kissinger's and Ozawa–Doyle's methods. Sensitivity tests revealed that the compound was insensitive to mechanical stimuli. In addition, the compound was explored as additive to promote thermal decomposition of ammonium perchlorate by differential scanning calorimetry.

Keywords: 5-Aminotetrazole; Pyridine-2,6-dicarboxylic acid; Crystal structure; Non-isothermal kinetics; Thermal decomposition; Ammonium perchlorate

1. Introduction

Research in highly energetic materials is directed towards the synthesis of simple molecules with high energy, high density, high heat resistance, and low sensitivity [1]. Considerable attention has been paid to the study of high-nitrogen heterocyclic materials as ligands to coordinate with metals because of the varied structures and favorable energetic properties [2–8]. 5-Aminotetrazole (HATZ), as a simple tetrazole derivative, has the highest nitrogen content (82.3wt %) among organic compounds, five nitrogen atoms being potentially metal binding. It has greater heat of formation and greater possibility for hydrogen bonding, giving the resulting compounds high thermal stability [9].

We are currently investigating the chemistry of simple tetrazole derivatives and carboxylic acids with respect to the continuing interest in high nitrogen compounds as ingredients for propellants and explosives [10, 11].

---

*Corresponding author. Email: sanpingchen@126.com

Ammonium perchlorate (AP) is the common oxidizer in composite solid propellants, and the thermal decomposition characteristics of AP directly influence the combustion behavior of solid propellants [12]. Many effective combustion catalysts for thermal decomposition of AP, such as metal oxides, which are not nitrogen-rich or energetic compounds, have been reported [13–16].

Copper(II) exhibits good ability to coordinate many different types of ligands and is more environmentally friendly than toxic heavy metal cations such as lead(II) and mercury(II). Pyridine-2,6-dicarboxylic acid is a useful ligand for constructing crystalline architectures due to its rigid and planar nature, and proton donating and accepting capabilities for hydrogen bonding [17]. In this article, we report the synthesis and structure of Cu(HATZ)(PDA)(H₂O), the thermal decomposition process, the kinetic parameters of the first exothermic process of the compound, the sensitivity, and the catalytic performance toward thermal decomposition of AP.

2. Experimental

General caution: HATZ and the title compound are energetic materials and tend to explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat and ear plugs) should be taken, especially when the compound is prepared on a large scale.

2.1. *Materials and instruments*

All reagents (analytic grade) were purchased commercially and used without purification. Elemental analyses were carried out using a Vario EL III analyzer. Infrared (IR) spectra were recorded on a Bruker FTIR instrument as KBr pellets. Thermogravimetric analysis and differential scanning calorimetry (DSC) were carried out on a Netzsch STA 449C instrument and a CDR-4P thermal analyzer of Shanghai Balance Instrument factory, respectively, using dry oxygen-free nitrogen with a flow rate of $10 \, \text{mL} \, \text{min}^{-1}$. The sample of about 0.5 mg was held in platinum pans for TG and sealed in aluminum pans for DSC. The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$) [18]. The friction sensitivity of the compound was determined on a Julius Peter's apparatus by following the BAM method [19].

2.2. *Synthesis of the compound*

An aqueous solution (10 mL) of Na₂PDA (0.021 g, 0.1 mmol) was slowly added to an aqueous solution (10 mL) containing both $Cu(NO_3)_2 \cdot 3H_2O$ (0.024 g, 0.1 mmol) and HATZ (0.035 g, 0.1 mmol) with stirring about 1 h. The resulting solution was filtered and evaporated slowly at room temperature for 5 days in a dark place. Blue block-like crystals suitable for X-ray analysis were obtained (yield 48%). Anal. Calcd (%) for $C_8H_8CuN_6O_5$: C, 28.97; H, 2.43; N, 25.33. Found: C, 28.85; H, 2.39; N, 25.18. IR data

Table 1. Crystal data and structure refinement parameters for the title compound.

Empirical formula	$C_8H_8CuN_6O_5$
Formula weight	331.74
Crystal system	Monoclinic
Space group	*C2/c*
Temperature (K)	298(2)
Unit cell dimensions (Å, °)	
a	25.735(2)
b	12.968(2)
c	7.158(1)
α	90
β	103.892(2)
γ	90
Volume (Å^3), *Z*	2318.9(5), 8
Calculated density (g cm^{-3})	1.900
Absorption coefficient (mm^{-1})	1.917
F(000)	1336
θ range for data collection (°)	1.63–24.99
Independent reflections	2041
Goodness-of-fit on F^2	1.000
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0503$, $wR_2 = 0.1240$
R indices (all data)	$R_1 = 0.0808$, $wR_2 = 0.1478$
Largest difference peak and hole (e Å^{-3})	0.762 and −0.810

(KBr pellet, cm^{-1}): 3487 s, 3238 s, 1704 m, 1618 s, 1596 s, 1433 m, 1359 w, 1347 m, 1282 s, 1276 s, 878 w, 763 m, 731 w, 649 w.

2.3. *X-ray crystallography*

The single crystal X-ray experiment was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scan mode. The single crystal structure was solved by direct methods and refined with full-matrix least-squares refinements based on F^2 using SHELXS 97 [20] and SHELXL 97 [21]. All non-H atoms were located using subsequent Fourier-difference methods. Hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent. Details of crystal data, data collection parameters, and refinement statistics are given in table 1. Selected bond lengths and angles of the compound are listed in table 2.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction shows the compound crystallizes in monoclinic space group *C2/c* and exists as a 3-D supramolecule. Figure 1 shows the molecular unit of Cu(HATZ)(PDA)(H$_2$O) with the atom labeling scheme. Cu(II) has a distorted square-pyramidal geometry, coordinated by two oxygen atoms and nitrogen from PDA (Cu(1)–N(1) = 1.898(5) Å, Cu(1)–O(1) = 2.022(4) Å, Cu(1)–O(3) = 2.043(4) Å), a ring nitrogen of HATZ (Cu(1)–N(2) = 1.934(5) Å), and water (Cu(1)–O(5) = 2.244(4) Å).

Table 2.   Selected bond lengths (Å) and angles (°) for the compound.

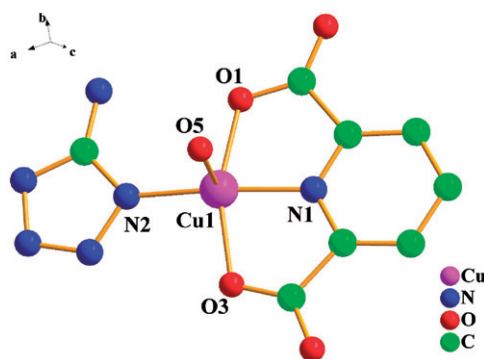|	
Cu(1)–N(1)	1.898(5)
Cu(1)–N(2)	1.934(5)
Cu(1)–O(1)	2.022(4)
Cu(1)–O(3)	2.043(4)
Cu(1)–O(5)	2.244(4)
N(1)–Cu(1)–N(2)	169.0(2)
N(1)–Cu(1)–O(1)	80.9(2)
N(2)–Cu(1)–O(1)	98.4(1)
N(1)–Cu(1)–O(3)	80.5(2)
N(2)–Cu(1)–O(3)	98.5(2)
O(1)–Cu(1)–O(3)	160.0(2)
N(1)–Cu(1)–O(5)	92.9(2)
N(2)–Cu(1)–O(5)	98.1(2)

Figure 1.   Molecular unit and labeling scheme; hydrogen atoms are omitted for clarity.

As shown in figure 2, the molecular unit is further extended into a 2-D supramolecular layer in the [1 1 0] plane through hydrogen bonds with O1, O2, O3, O4, and N3 as hydrogen-bond acceptors to interact with hydrogen-bond donors N6, C3, N5, N5, and N6 from the adjacent molecule. Hydrogen bond details are given in table S1.

Coordinated water acts as a hydrogen-bond donor to interact with acceptors N4 and O2 from the adjacent 2-D supramolecular layer. The title compound is thus assembled into a 3-D supramolecular structure through these hydrogen bonds (figure 3).

Like Cu(HATZ)(PDA)(H₂O), the energetic compound Bi(tza)₃ [6] (Htza = tetrazole acetic acid) possesses abundant intramolecular hydrogen bonds *via* N–H and O–H. All the hydrogen bonds in different layers of Bi(tza)₃ make the molecules pack into a layered structure.

3.2.   *Thermal decomposition*

The DSC and TG–DTG curves at the linear heating rate of $10°C\,min^{-1}$ under nitrogen are shown in figures 4 and 5 to demonstrate the thermal decomposition processes of Cu(HATZ)(PDA)(H₂O). In the DSC curve, there is one endothermic process and two
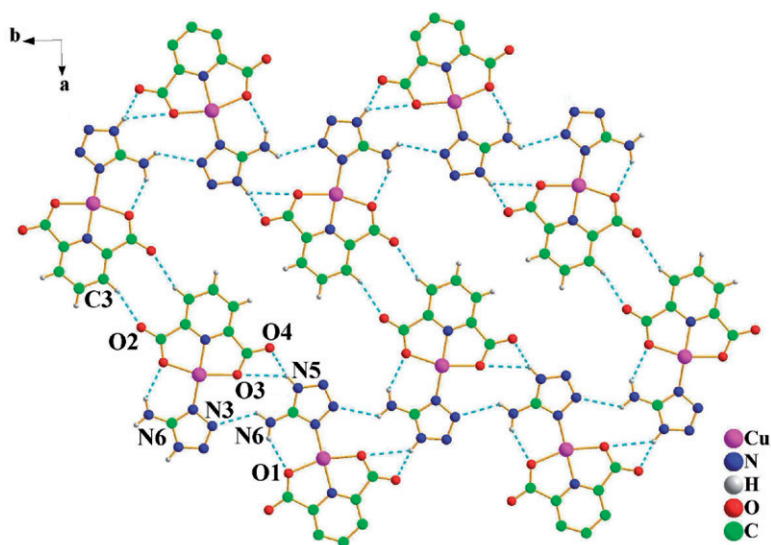
Figure 2.   2-D supermolecular structure for the compound.
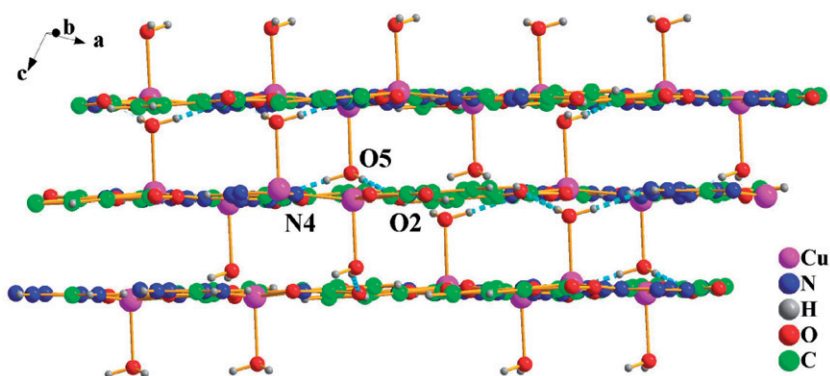

Figure 3.   3-D supermolecular structure for the compound.
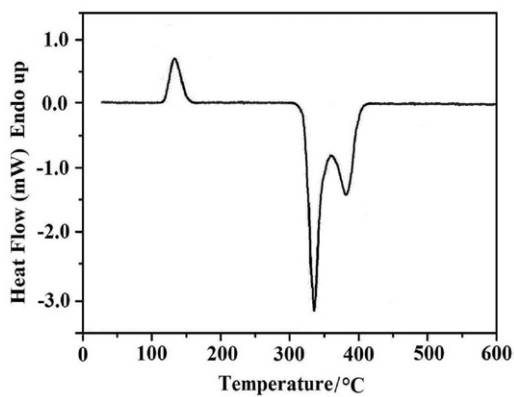

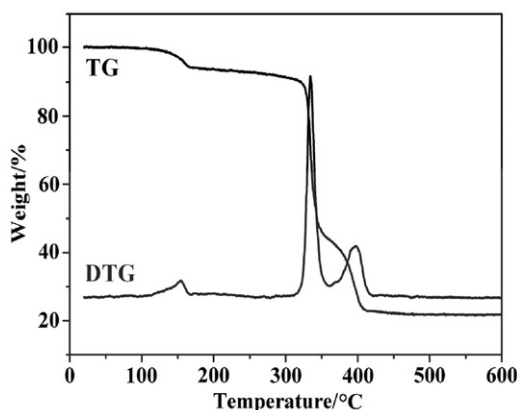Figure 4.   DSC curve for the compound.

Figure 5.   TG-DTG curves for the compound.

intense exothermic processes from 110°C to 420°C. The endothermic process starts at 110°C and ends at 160°C. Because the two intense exothermic decomposition processes occur successively, one decomposition process does not finish, and another occurs, the exothermic peaks cannot be separated, and form a wide exothermic peak. The first exothermic decomposition process occurs at 310°C and ends at about 360°C; the second exothermic decomposition process occurs at the same time and ends at about 420°C.

In the TG–DTG curves, there are three successive weight loss stages from 110°C to 420°C, which correspond to the three processes in the DSC curve. The first weight loss stage starts at 110°C and ends at 160°C with weight loss percentage of 5.90% for loss of coordinated water (5.44%, Calcd). From 160°C to 310°C, the weight remains constant. After this, the compound goes through two consecutive weight loss processes from 310°C to 420°C, which are considered to be loss of HATZ and PDA. Then the compound completely converts to CuO with residue percentage of 23.85%, in agreement with the calculated value 24.17%. CuO is demonstrated by X-ray powder diffraction analysis (figure S1).

3.3. *Non-isothermal kinetics analysis*

In the present work, Kissinger's method [22] and Ozawa–Doyle's method [23, 24] are used to determine the apparent activation energy (E) and the pre-exponential factor (A). The Kissinger and Ozawa–Doyle equations are as follows.

$$\frac{\mathrm{d}\ln \frac{\beta}{T_p^2}}{\mathrm{d}\frac{1}{T_p}} = -\frac{E}{R} \tag{1}$$

$$\log \beta + \frac{0.4567E}{RT_p} = C \tag{2}$$

where T_p is the peak temperature; A is the pre-exponential factor; E is the apparent activation energy; R is the gas constant; β is the linear heating rate and C is constant.

Table 3.   The peak temperatures of the first exothermic stage at different heating rates and the kinetic parameters.

Heating rates ($^\circ$C min^{-1})	Peak temperature ($^\circ$C)
5	342.5
10	349.2
15	352.6
20	356.1
25	358.7
Calculation results by Kissinger's method E_k (kJ mol^{-1})	314.0
log A_k (s^{-1})	24.57
Linear correlation coefficient (R_k)	0.9984
Calculation results by Ozawa–Doyle's method E_o (kJ mol^{-1})	308.5
Linear correlation coefficient (R_o)	0.9985

Based on the first exothermic peak temperatures measured at five different heating rates of 5, 10, 15, 20, and 25°C min^{-1}, Kissinger's and Ozawa–Doyle's method are applied to study the kinetics parameters of Cu(HATZ)(PDA)(H$_2$O). From the original data, the apparent activation energy E_k and E_o, pre-exponential factor A_k and linear correlation coefficients R_k and R_o are determined (table 3).

3.4. Sensitivity test

Impact sensitivity of Cu(HATZ)(PDA)(H$_2$O) was tested using a 2 kg drop hammer and calculated value of H$_{50}$ represented the drop height of 50% initiation probability. The impact sensitivity value (H$_{50}$) of the compound was 164 cm, which corresponds to impact energy of 32.1 J. Under the same test conditions, the impact sensitivity value (H$_{50}$) of TNT was 76.5 cm (15.0 J), consistent with the value reported [25]. Therefore, the impact sensitivity of the title compound was lower than that of TNT.

Friction sensitivity of the compound was measured by applying a Julius-Peter's machine. No friction sensitivity was observed up to 353 N. The friction sensitivity of the compound was far lower than that of RDX (118 N) [26].

As observed with [Bi(tza)$_3$]$_n$ [6], K(2,4-DNI), Rb(2,4-DNI)(2,4-HDNI)(H$_2$O)$_2$ and Ba(2,4-DNI)$_2$(H$_2$O)$_4$ (2,4-HDNI = 2,4-dinitroimidazole) [7], the low sensitivity is attributed to intramolecular hydrogen bonds occurring in these compounds.

3.5. Effects on thermal decomposition of AP

Cu(HATZ)(PDA)(H$_2$O) is explored as a promoter of thermal decomposition of AP, the key component of composite solid propellant. The performance of the compound on the thermal decomposition of AP (compound and AP were mixed at a mass ratio of 1:3) was investigated by DSC measurement with a heating rate of 10°C min^{-1} in N$_2$ atmosphere from 100°C to 500°C with Al$_2$O$_3$ as reference. The total sample mass used was less than 1.0 mg for all runs. Figure 6 shows the DSC curves of both AP and the mixture of AP with the compound. The endothermic peak of AP at 242°C is due to the crystal transformation of AP from orthorhombic to cubic phase [27]. The exothermic peaks at 335°C and 440°C are attributed to partial decomposition of AP to form some intermediate product and then complete decomposition to volatile products [28, 29],
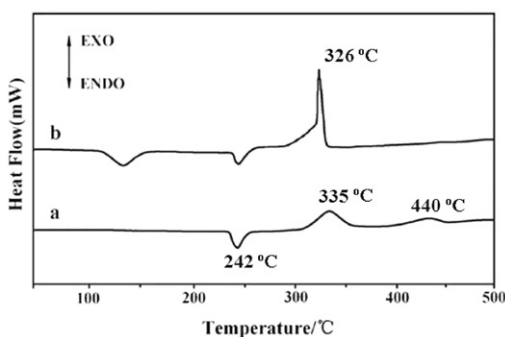
Figure 6. DSC curves for AP (a) and AP + Compound (b).

corresponding to heat of $1.47 \, \text{kJ g}^{-1}$ and $0.68 \, \text{kJ g}^{-1}$, respectively. From figure 6(b), we can see that the compound has no significant impact on the phase transition of AP. The two exothermic peaks merge to one and the peak temperature ($326°C$) is lower than the exothermic peak temperature of pure AP ($335°C$). The sharp exothermic peak indicates a rapid decomposition process and the decomposition heat increases dramatically from 1.47 to $3.11 \, \text{kJ g}^{-1}$. The compound decomposes and releases heat itself which enhances the total heat of the mixture, as well as the formation of metal at the molecular level on the propellant surface which may contribute toward the catalytic effect [30]. Obviously, AP decomposition is accelerated in the presence of Cu(HATZ)(PDA)(H₂O).

4. Conclusion

We report the synthesis and structure analysis of a 3-D energetic compound, Cu(HATZ)(PDA)(H₂O). Extensive hydrogen bonding in the solid state structure makes the title compound insensitive to impact and friction stimuli. DSC experiments reveal that the compound accelerates the decomposition of AP, which could make the compound useful in propellants.

Supplementary material

CCDC 697532 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The CuO X-ray powder diffraction data and H-bond table are available.

Acknowledgments

References

[1] G. Singh, S.P. Felix. *J. Hazard. Mater.*, **90**, 1 (2002).
[2] T.M. Klapötke, C.M. Sabate, A. Penger, M. Rusan, J.M. Welch. *Eur. J. Inorg. Chem.*, 880 (2009).
[3] T.M. Klapötke, J. Stierstorfer, B. Weber. *Inorg. Chim. Acta*, **362**, 2311 (2009).
[4] W.T. Wang, S.P. Chen, G. Fan, G. Xie, B.J. Jiao, S.L. Gao. *J. Coord. Chem.*, **62**, 1879 (2009).
[5] Y. Cui, J.G. Zhang, T.L. Zhang, L. Yang, J. Zhang, X.C. Hu. *J. Hazard. Mater.*, **160**, 45 (2008).
[6] S.W. Wang, L. Yang, T.L. Zhang, G.T. Zhang, J.G. Zhang, Z.N. Zhou. *J. Coord. Chem.*, **64**, 2583 (2011).
[7] G.F. Zhang, Y. Wang, M.Y. Cai, D.M. Dai, K. Yan, A.S. Ma, P. Chen, R. Wang, P. Li, J.H. Yi, F.Q. Zhao, J.Z. Li, X.Z. Fan. *J. Coord. Chem.*, **63**, 1480 (2010).
[8] F. Guan, Z.Y. Li, S.J. Juan, Z.M. Yan. *J. Coord. Chem.*, **64**, 3711 (2011).
[9] X.W. Wang, J.Z. Chen, J.H. Liu. *Cryst. Growth Des.*, **7**, 1227 (2007).
[10] Q. Yang, S.P. Chen, S.L. Gao. *Inorg. Chem. Commun.*, **12**, 1224 (2009).
[11] Q. Yang, S.P. Chen, G. Xie, S.L. Gao. *J. Hazard. Mater.*, **197**, 199 (2011).
[12] M. Friedrich, J.C. Gálvez-Ruiz, T.M. Klapötke, P. Mayer, B. Weber, J.J. Weigand. *Inorg. Chem.*, **44**, 8044 (2005).
[13] M. Zheng, Z.S. Wang, J.Q. Wu, Q. Wang. *J. Nanopart. Res.*, **12**, 2211 (2010).
[14] X.F. Sun, X.Q. Qiu, L.P. Li, G.S. Li. *Inorg. Chem.*, **47**, 4146 (2008).
[15] H.B. Liu, Q.Z. Jiao, Y. Zhao, H.S. Li, C.B. Sun, X.F. Li, H.Y. Wu. *Mater. Lett.*, **64**, 1698 (2008).
[16] L.J. Chen, G.S. Li, L.P. Li. *J. Therm. Anal. Calorim.*, **91**, 581 (2008).
[17] L. Wang, L. Duan, E. Wong, D. Xiao, Y. Li, Y. Lan, L. Xu, C. Hu. *Transition Met. Chem.*, **29**, 212 (2004).
[18] R. Meyer, J. Kohler. *Explosives*, 4th Edn, VCH Publishers, New York (1993).
[19] R. Meyer, J. Kohler. *Explosives*, 4th Edn, VCH Publishers, New York (1993).
[20] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Göttingen, Göttingen, Germany (1997).
[21] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).
[22] H.E. Kissinger. *Anal. Chem.*, **29**, 1702 (1957).
[23] T. Ozawa. *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
[24] C.D.J. Doyle. *J. Appl. Polym. Sci.*, **5**, 285 (1691).
[25] J. Koehler, R. Meyer. *Explosivstoffe*, 9th Edn, Wiley-VCH, Weinheim, Germany (1998).
[26] M. Anniyappan, M.B. Stalwart, G.M. Gore, S. Venugopalan, B.R. Gandhe. *J. Hazard. Mater.*, **B137**, 812 (2006).
[27] J.A. Creighton, D.G. Eadon. *J. Chem. Soc. Faraday Trans.*, **87**, 3881 (1991).
[28] W.A. Rosser, S.H. Inami. *Combust. Flame*, **12**, 427 (1968).
[29] P.W.M. Jacobsete, G.S. Pearson. *Combust. Flame*, **13**, 419 (1969).
[30] P.B. Kulkarni, T.S. Reddy, J.K. Nair, A.N. Nazare, M.B. Talawar, T. Mukundan, S.N. Asthana. *J. Hazard. Mater.*, **123**, 54 (2005).