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Salts of Perchlorylamide as a Novel Class of Light-sensitive Explosive for Laser Initiation

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The first papers concerning the synthesis and properties of perchlorylamide were published about 40 years ago[1,2]. But up to now, the salts of perchlorylamide are relatively little-known substances. They can be synthesized by two alternative methods. The first method is the ammonolysis of perchloryfluoride:

$$ClO_3F + 3NH_3 \longrightarrow NH_4F + \underset{(I)}{NH_4NHClO_3} \quad (1)$$

Salt Ⅰ is a precursor for the preparation of other perchlorylamide salts. For example, salt Ⅱ can be synthesized by the following reaction:

$$\underset{(I)}{NH_4NHClO_3} + 2KOH \longrightarrow \underset{(II)}{K_2NClO_3} + NH_4OH + H_2O \quad (2)$$

Reaction (1) is carried out at −78℃. The second method for preparing salt Ⅰ is the ammonolysis of chloro oxide in carbon tetrachloride as solvent[3]:

$$Cl_2O_7 + 2NH_3 \longrightarrow \underset{(III)}{NH_2ClO_3} + NH_4ClO_4 \quad (3)$$

Perchlorylamide (Ⅲ) gives salt Ⅰ with the excess of ammonia. Perchlorylamide (Ⅲ) is a dibasic acid with $pKa_1 = 5.64 \pm 0.04$ and $pKa_2 = 11.95 \pm 0.03$. Acidic salts of Ⅲ undergo hydrolytic decomposition in the air, whereas neutral salts are not hydrolized under this condition. Acidic salts of Ⅲ are more hygroscopic than the neutral salts. Thermal stability of the salts of Ⅲ decreases in the following sequence:

$$K_2NClO_3 > BaNClO_3 > SrNClO_3 > Na_2NClO_3 > KHNClO_3$$

Fast heating of the perchlorylamide salts causes explosion[4,5]. $BaNClO_3$ (Ⅳ) undergoes a thermal decomposition in two main pathways:

$$2\underset{(IV)}{BaNClO_3} \longrightarrow Ba(NO_3)_2 + BaCl_2 \quad (4)$$

$$2\underset{(IV)}{BaNClO_3} \longrightarrow BaO + BaCl_2 + 2.5O_2 + N_2 \quad (5)$$

The contribution of reaction (5) increases with acceleration of heating. Detectable amount of $KClO_3$ is formed during salt Ⅱ thermal decomposition. The salts of Ⅲ are sen-sitive to impact and friction and can initiate detonation in high explosives[6]. Studies on the spectra of crystalline salts of Ⅲ and their aqueous solution show that in the salts of alkaline and alkaline earth metals metal-anion bonds are ionic in nature[7]. The ion $NClO_3^{2-}$ has tetrahedral configuration and the structure of perchlorylamide salts are analogous to those of the corresponding salts of sulfuric acid[8]. The reactivity of the salts of Ⅲ exceeds that of perchlorate salts. Thus, the perchlorylamide salts react with Zn, $NaNO_2$, KI, $FeSO_4$[8].

We supposed that the salts of Ⅲ may be light-sensitive explosives having a low threshold of laser beam initiation. This supposition was based on the high reactivity of the 5-aminotetrazolate complex of silver perchlorylamide[9] having extremely high sensitivity to laser beam radiation, and the mechanism of dianion Ⅲ thermal decomposition.

The sensitivities of salts Ⅱ and Ⅳ to laser beam radiation ($\lambda = 1060$nm, τ about 25ns) have been studied. The diameter of the laser beam was about 4mm. The total energy of the laser beam pulse was near 40mJ. The study of the sensitivity to laser beam radiation was carried out according

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to the procedure published in [10,11]. Light-sensitive explosive sheets (about $1cm^2$) were formed and tested. The sheets containd about $50mg/cm^2$ of metal salts Ⅱ or Ⅳ bonded by an optically transparent polymer. The polymer content in the explosive composition approached 10%. The threshold of the initiation of salt Ⅱ was near $0.1J/cm^2$, for salt Ⅳ 5 ~ $7mJ/cm^2$. The calculation error of the initiation thresholds was near 20%. Thus, two novel light-sensitive explosive compositions have been worked out. These compositions have lower thresholds of initiation than that of pressed charges of lead azide.

The ballistic pendulum was used for measuring the bonding impulse of explosive films containing light-sensitive salt Ⅳ. The measurment accuracy was within 7%. The charges used had the same diameter and composition as those used in the study of light-sensitivity thresholds. Laser beam was defocused in such a way that the energy density in the center of samples was 20% higher than that on the periphery. The average concentration of laser beam energy on the surface of samples was twice as high as the threshold of laser initiation. Consequently, the averge energy density in the laser beam was not less than $10mJ/cm^2$. The planar initiation of the charges was realized in all cases. The implus density J_s (dyne · s/cm^2) of the explosion products is related to the explosive unit square mass m_s (mg/cm^2) by a simple equation which is analogous to that published in [12]:

$$J_s = (162.9 \pm 10.1) \times m_s - (7918.4 \pm 1171.8) \quad (6)$$
$$r = 0.985, n = 10$$

Where r — correlation coefficient, n — number of experimental points. Equation (6) show that a fraction of the explosive doesn't contribute to the registered loading impact. The portion of the explosive is likely to be consumed in the deflagration-to-detonation transition process. Still it is possible that thin layers of explosive films have higher thresholds of initiation than thick one and they can not be ignited at the levels laser beam energy used in our experiments[9].

REFERENCES:

[1] Engelbrcht A, Atzwanger H. J. Inorg. Nucl. Chem., 1956,2: 348.

[2] Mandell H C, Barth-Wehrenalp G. J. Inorg. Nucl. Chem.,1959,12: 90.

[3] Vast M P C R. Acad. Sci. Paris. Ser. C-1972-T.274.

[4] Rosolovskii V Ya, Kolesnikov I V. J. Inorg. Chem., 1968,13(1): 180 (in Russian).

[5] Rosolovskii V Ya, Kolesnikov I V. J. Inorg. Chem., 1969,14(11): 2917 (in Russian).

[6] Taranoushych V A. Proceedings of XVI Mendeleev Cohgress on General and Applied Chemistry[C]. Moscow,1998,2: 460.

[7] IR-specra in inorganic chemistry. Ed. Yu. Ya. Kharitonov-M: Nayka-1971 – 182 (in Russian).

[8] Rosolovskii V Ya, Kolesnikov I V. J. Inorg. Chem., 1968,13(5): 1290 (in Russian).

[9] Ilyushin M A,Tselinskii I V,Petrova N A,et al. Laser initiation of pressed light-sensitive explosive and sheet[J]. HANNENG CAILIAO,1995,3(1): 22 ~ 25.

[10] Chernai A V, Sobolev V V,Ilyushin M A,et al. Combust. Explos.,1994,30(2): 106 (in Russian).

[11] Chernai A V, Sobolev V V,Ilyushin M A. Phys. Techn. High Pressure,1995(4): 62 (in Russian).

[12] Ilyushin M A,Petrova N A,Tselinskii I V. The correlation between thermal decomposition and laser ignition parameters for complexes of HAT[J]. HANNENG CAILIAO, 1993,1(4): 41 ~ 43.

用于激光起爆的新型光敏炸药——过氯酰胺

摘要: 介绍了过氯酰胺盐的一些性质,指出过氯酰胺盐是激光起爆阈值低的光敏炸药。用10%光学透明的聚合物分别粘结 $50mg/cm^2$ 的过氯酰胺钾(Ⅱ)和过氯酰胺钡(Ⅳ)制成了 $1cm^2$ 的光敏炸药薄板并进行了实验。Ⅱ的起爆阈值约 $0.1J/cm^2$,Ⅳ的起爆阈值为 5 ~ $7mJ/cm^2$,皆低于压装的叠氮化铅药柱。全都实现了平面起爆。

关键词: 过氯酰胺; 光敏炸药; 激光起爆

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