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THE BURNING OF AMMINE PERCHLORATES AND NITRATES OF COPPER (II) NICKEL (II) AND COBALT (III)

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Foreign Technology Division Wright-Patterson Air Force Base, Obio

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THE BURNING OF AMMINE PERCHLORATES AND NITRATES OF COPPER (II) NICKEL (II) AND COBALT (III)

V. V. Gorbunov, A. A. Shidlovskiy and L. F. Shmazin (Moscow)

Complex perchlorates and nitrates of copper, nickel and cobalt serving in the capacity of ligands of ammonia molecules, are capable of electrothermic decomposition and exhibit explosive properties [1-3]. The authors [4] have pointed out that nitrates of hexammine cobalt (III) and of tetrammine copper (II) burn with an increasing pressure.

The effect of pressure on the combustion rate of complex perchlorates and nitrates of copper, nickel and cobalt were studied using the general formula

 $[Me^{+m} (NH_3)_x] \cdot (AH)_m$, where $AH - ClO'_4, NO'_3$, $A = ClO'_4 - MS'_3$

and x = 6; 4 or 2. The salts were studied according to procedures described in [5] and analyzed for the ammonia content. The combustion rate of the salts under pressure to 100 atm in an atmosphere of nitrogen was determined. The materials were placed in plexiglass tubes with an inside diameter of 7 mm (in the case of rapid-burning

copper and cobalt perchlorates - 4 mm); the relative density of the charges was 0.85-0.95. The charge was ignited by an electric coil, and the combustion rate was determined by a photorecorder.

The calculated results of the heat and temperature of combustion of the investigated salts based on the gross-weight formulas of the combustion reaction and the experimental results based on their combustion rates are presented in the table.

(1)		- A	Продукты реакции горевня			С.9 Теплота горения		TeMn.	. npm	
Формуль соли	анал. тепр.	Н 298 ккал! моль (5)	H ₂ O _{nap}	N _s	0,	прочие (8)	(10 ккал моль	KRAI KZ	Pacyerii.	Ck. rop 60 ami.,2
[Cu(NH ₃) ₄](ClO ₄) ₂	3)1(4) 20,5,20,6	158*	6	2	1	CuCl _p +0,5Cl ₂	183	555	112 20(0	18,3
[Co(NH3)6] (CIO4)3	22,622,2	247[6]	9	3	1,5	CoCl2 +0,5Cl2	316	685	2010	11,7
[Ni(NH ₃) 6] (CIO ₄) 2	28,3 28,4	227*	8	3	-	NiCl2r+H:	260	723	2050	1,90
[Cu(NH ₃) ₄] (NO ₃) ₂	25,926,6	198[6]	6	3	-	Cum	154	605	1750	0,98
[Ni(NH ₃) ₄](NO ₃) ₂	27,6 27,1	218*	υ	3		Ni	126	503	1530	0,63
[Co(NH ₃) ₆] (NO ₃) ₃	28,7 29.4	306[6]	9	4,5	-	Co	214	617	1680	0,57
[Cu(NH ₃) ₂](NO ₂) ₂	15,415,3	140[7]	3	2	1	Cuo	73	331	1300	0,30
[Ni (NH3)2] (NO3)2	15,7 15,7	160*	3	2	1	Nio	70	322	1270	0,21
[Ni (NH3)6] (NO3)2	35,7 35,8	267*	6	3	-	Ni+2NI13	102	358	1100	0,11

• Определены методы сравнительного расчета. (14)

KEY: (1) Formula of the salt; (2) NH_3 content, % by weight; (3) Analytical; (4) Theoretical; (5) kcal/mole; (6) Products of the combustion reaction; (7) H_2^{O} vapor; (8) remainder; (9) Heat of combustion; (10) kcal/mole; (11) kcal/kg; (12) Calc. temp. of combustion; (13) combustion rate at 60 atm, g/cm² s; (14) *Determined by the methods of comparative analysis.

The combustion rate of ammine perchlorates of copper, nickel and cobalt increases linearly with an increase in pressure from 200 to 100 atm (Fig. 1). At pressures of 1-20 atm the investigated perchlorates exhibit a varied nature. For the most rapidlyburning one, $[Cu(NH_3)_4](ClO_4)_2$ the combustion rate during the transition from 15 to 13 atm is reduced by one-half, at 10.8 and 5 atm the combustion of this salt ceased after removing the igniting coil, and stable combustion was observed at 1 atm. The combustion

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Fig. 1. The effect of pressure on the combustion rate of ammine perchlorates of copper, nickel and cobalt. $1 - [Cu(NH_3)_4](ClO_4)_2;$ $2 - [CO(NH_3)_6](ClO_4)_3; 3 - [Ni(NH_3)_6](ClO_4)_2.$

rate of $[CO(NH_3)_6](ClO_4)_3$ drops sharply with the lowering of the pressure from 20 down to 16 atm, and then decreases linearly in the interval of 16-1 atm. As for the comparatively clow combustion rate of $[Ni(NH_3)_6](ClO_4)_2$ it increases linearly throughout the interval of pressures from 1 to 100 atm.

The dependence of the combustion rate on the pressure for the ammine nitrates of copper, nickel and cobalt is presented in (Fig. 2). The highest combustion rate was observed for $[Cu(NH_3)_4]$ $(NO_3)_2$. Only this salt burned at p = 1 under experimental conditions. Burning somewhat slower was $[Ni(NH_3)_4]$; the solid products of its combustion remained in the form of a porous nickel rod.

The diammines of copper and nickel nitrates burned considerably more slowly. The solid products of their combustion contained a significant amount of metallic oxides, especially at high pressures. An analysis of the condensed residue of combustion of $[Cu(NH_3)_2]$ $(NO_3)_2$ indicated that at 100 atm the copper oxide content amounted to 90-95%, at 6 atm - about 50%.

The hexammine nitrate of nickel was slowest burning with a faint dark-red color. After the burning of the charge a porous nickel rod remained.



Fig. 2. The effect of pressure on the combustion rate of ammine nitrates of copper, nickel and cobalt. $1 - [Cu(NH_3)_4](NO_3)_2;$ $2 - [Ni(NH_3)_4](NO_3)_2; 3 - [Co(NH_3)_6](NO_3)_2; 4 - [Cu(NH_3)_2](NO_3)_2;$ $(NO_3)_2; 5 - [Ni(NH_3)_2](NO_3)_2;$ $6 - [Ni(NH_3)_6](NO_3)_2.$

It is known that the first stage of decomposition of the studied complexes is the separation of ammonia, after which the decomposition of the remaining salts occurs. The exothermic effect in this case is governed by the oxidation of the ammonia with gaseous products of the decomposition of the hydroxy anion. The heat release rate, and consequently, the combustion rate of the ammines will depend on the activity of the forming oxidizer-gases and on the combustion temperature. A comparison of the combustion rates of perchlorates and nitrates with the similar named complex cations indicates that perchlorates burn approximately 20 times faster than nitrates. This difference in the combustion rates should be attributed to the faster oxidative activity of the products of decomposition and to the combustion temperature of the perchlorates.

We varied the combustion temperature of the ammines with a change in the ligand-oxidizer ratio for a number of hexa-, tetraand diammines. For the nitrates of copper and nickel ammines with a different content of ammonia the combustion rate increases with a rise in the combustion temperature (see table). During combustion in the gaseous phase the relationship $\lg \frac{u_m^2}{m_3} - \frac{1}{T_c}$ should be linear

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Fig. 3. The dependence of the combustion rate of ammine nitrates of copper and nickel at 60 atm on the calculated combustion temperature. 1 - $[Cu(NH_3)_4](NO_3)_2; 2 [Ni(NH_3)_4](NO_3)_2; 3 - [Cu(NH_3)_2]$ $(NO_3)_2; 4 - [N1(NH_3)_2](NO_3)_2;$ $5 - [Ni(NH_3)_6](NO_3)_2.$

[8]. At the indicated coordinates our data satisfactorily falls along a straight line (Fig. 3), the slope of which provides the activation energy of the combustion reaction of about 38 kcal/mole. This value is close to the activation energy of the catalytic oxidation of ammonia - 34 kcal/mole [9].

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