BURNING OF COPPER (II) TETRAMINE SALTS

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It was shown in [1] that the burning rate of perchlorates of amines of copper (II), nickel (II), and cobalt (III) is 15-20 times greater than the burning rate of nitrates of the same amines.

In the present study we investigated the burning of complex salts of copper (II) tetramine (CTA) having the general formula

$$[Cu(NH_3)_4](An)_2,$$

where

$$An - BrO_3^-;\ ClO_3^-;\ ClO_4^-;\ MnO_4^-;\ NO_3^-;\ NO_2^-\ \text{and}\ IO_3^-.$$

The complex salts were obtained by methods analogous to those described in [2] and were analyzed for content of copper and ammonia. Charges with a relative density of not less than 0.90 pressed into Plexiglas tubes with a diameter of 7 or 4 mm were used. The experiments were conducted in a constant-pressure bomb in a nitrogen atmosphere at pressures to 100 gauge atm. The burning rate was measured by means of a streak camera. Thermal stability of the complex salts was estimated on the basis of the ignition delay time (τ_{del}) of a 0.05 g sample at a temperature of 280°C.

The results of the experiments and calculations of the heat and temperature of combustion are given in Table 1 and Fig. 1.

In the investigated pressure range CTA bromate had the maximum burning rate. At pressures of 20-100 gauge atm CTA chlorate and perchlorate were close in burning rate and inferior in this respect to CTA bromate. At atmospheric pressure CTA bromate, chlorate, and perchlorate burn at rates of 3.0, 1.8, and

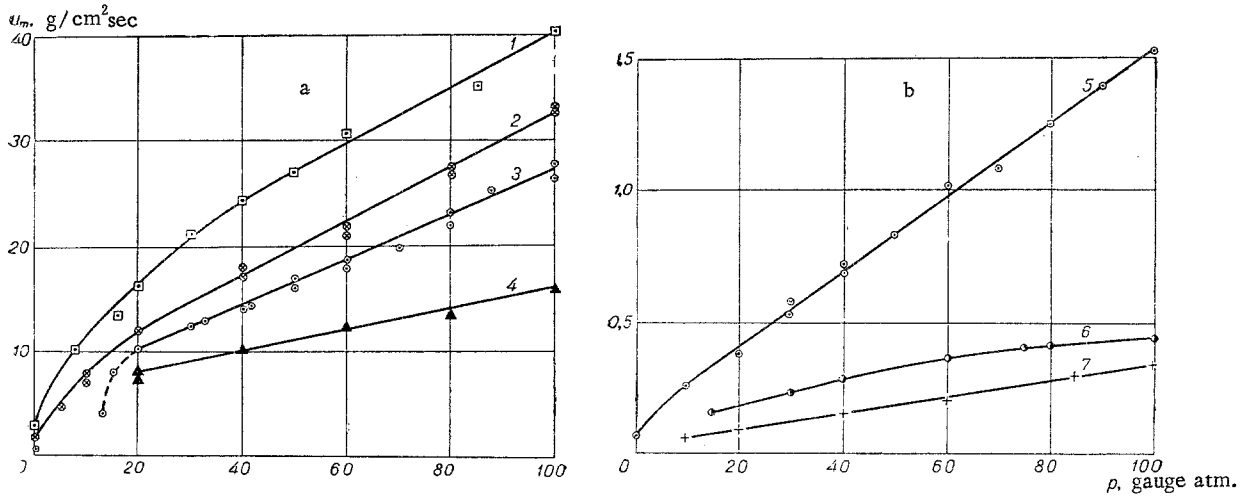

Fig. 1. Pressure dependence of the burning rate of copper (II) tetramine salts. a) Fast-burning salts of anions: 1) BrO_3^-; 2) ClO_3^-; 3) ClO_4^-; 4) MnO_4^-; b) slow-burning salts of anions: 5) NO_3^-; 6) NO_2^-; 7) IO_3^-.

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TABLE 1

Formula of salt	Purity of product, wt.%	$-\Delta H_{298}^{\circ}$ of formation, kcal/mole	Equation of burning reaction	Heat of combustion		Calc. comb. temp., °K	U_m, g/cm² sec at 100 gauge atm	τ_{del}, sec at 280°C
				kcal/mole	kcal/kg			
$[Cu(NH_3)_4](BrO_3)_2$	98,0	133	$=CuBr_{(g)}+6H_2O_{(g)}+0{,}5Br_{2(g)}+2N_2$	200	516	2150	40,5	Less than 1 sec
$[Cu(NH_3)_4](ClO_3)_2$	98,5	145	$=CuCl_{(g)}+6H_2O_{(g)}+0{,}5Cl_2+2N_2$	196	657	2100	33	"
$[Cu(NH_3)_4](ClO_4)_2$	99,5	158	$=CuCl_{(g)}+6H_2O_{(g)}+O_2+0{,}5Cl_2+2N_2$	183	555	1950	27	42±3
$[Cu(NH_3)_4](MnO_4)_2$	95,5	355	$=Cu+0{,}66Mn_3O_4+5{,}34H_2O_{(l)}+0{,}44NH_3+1{,}78N_2$	152	412	1500	16	Less than 1 sec
$[Cu(NH_3)_4](NO_3)_2$	99,5	198(3)	$=Cu+6H_2O_{(l)}+3N_2$	154	605	1750	1,5	44±2
$[Cu(NH_3)_4](NO_2)_2$	99,0	148	$=Cu+4H_2O_{(l)}+1{,}33NH_3+2{,}33N_2$	98	437	1350	0,44	5
$[Cu(NH_3)_4](JO_3)_2$	99,0	212	$=CuJ_{(g)}+0{,}5J_{2(g)}+6H_2O_{(g)}+2N_2$	107	225	1480	0,34	3

*The enthalpies of formation of the complex salts (except nitrate) were determined by the method of comparative calculation with respect to ΔH of the formation of the complex salt and corresponding simple salt taken from [3, 4].

0.6 g/cm^2 · sec, respectively. Copper tetramine permanganate begins to burn at 8 tech. atm; at higher pressures its burning rate is almost half that of perchlorate. Copper tetramine nitrate, nitrite, and iodate burn considerably more slowly. Of these salts only nitrate burns at atmospheric pressure (u_m = 0.7 g/cm^2 · sec); nitrite and iodate begin to burn at 15 and 10 tech. atm, respectively.

Strong ignition with a sharp sound was observed for the complex salts BrO_3^-, ClO_3^-, and ClO_4^- and mild ignition with a dark-red glow for MnO_4^-; CTA nitrate and nitrite decomposed with evolution of nitrogen oxides and iodate with the liberation of iodine vapors. The least stable was $[Cu(NH_3)_4](MnO_4)_2$, which at normal temperature decomposed with the formation of a loose residue consisting of CuO and MnO_2. Apparently the decomposition of this salt occurred also during the course of synthesis, as a consequence of which the purity of the product obtained was low (95.5%).

The investigated complex salts can be divided into two groups according to the burning rate: fast-burning salts with anions BrO_3^-, ClO_3^-, ClO_4^-, and MnO_4^-, whose burning rate at 100 tech. atm is within 40-16 g/cm^2 · sec, and slow-burning salts with anions NO_3^-, NO_2^-, and IO_3^-, whose burning rate at the same pressure is 1.5-0.34 g/cm^2 · sec, i.e., 1-2 orders less. The indicated differences are retained also at lower pressures.

A comparison of the burning rates and calculated combustion temperatures of the fast- and slow-burning complex salts showed that the latter have a lower combustion temperature. The exception is the fast-burning $[Cu(NH_3)_4](MnO_4)_2$ whose combustion temperature (1500°K) is lower than that of the slow-burning nitrate (1750°K). Evidently in the given case the lower combustion temperature is compensated by the considerably higher oxidative activity of the permanganate ion (or products of its decomposition) in comparison with the nitrate ion. The thermal stability of the complex salts does not have a substantial effect on their burning rate: in the group of fast-burning salts there are unstable salts ClO_3^-, BrO_3^-, and MnO_4^- (τ_{del} less than 1 sec) along with stable perchlorate (τ_{del} about 40 sec).

LITERATURE CITED

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