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Tetraamminecopper Perchlorate (TACP): Explosive Properties

Ondřej Vodochodský,[a] Martin Künzel,[b] Robert Matyáš,*[a] Jinřich Kučera,[a] and Jiri Pachman[a]

Abstract: Tetraamminecopper perchlorate (TACP) is one of the most interesting explosive copper perchlorate-ammonia complexes. Despite the fact that this complex has been known for more than 100 years there is very little information in the literature about its detonation parameters. Impact sensitivity of TACP is slightly higher than that for PETN while friction sensitivity is between those for PETN and RDX. Detonation velocity for infinite diameter is 3230 $m\,s^{-1}$ (density 0.9 $g\,cm^{-3}$). Critical diameter of TACP is low – less than 2 mm. Based on the heat of combustion measurement the previously published erroneous enthalpy of formation was corrected to −496 $kJ\,mol^{-1}$. Detonation heat of TACP is 4322 $kJ\,kg^{-1}$ and Gurney velocity is 1536 $m\,s^{-1}$. Experimentally measured detonation parameters of TACP were also compared with theoretically calculated values by the EXPLO5 code.

Keywords: Tetraamminecopper perchlorate · TACP · Detonation parameters · Detonation calorimetry · Sensitivity

1 Introduction

Cupric perchlorate forms various coordination compounds with ammonia which differ in the number of ammonia ligands or by having other ligands. The characterization of these copper perchlorate complexes and the mutual chemical transformations among them were investigated in the first third of the 20th century [1–4]. The first copper perchlorate-ammonia complex was probably prepared by Henry Roscoe in 1862. Roscoe described the formation of dark blue crystals by dissolving copper carbonate in perchloric acid, saturating this solution with gaseous ammonia and precipitating the final product by addition of ethanol [5]. However, Roscoe described the chemical formula of his product incorrectly. Based on the opinion of other chemists who later examined the chemical properties of various copper perchlorate-ammonia complexes in detail, Roscoe actually prepared $[Cu(NH_3)_4(H_2O)_2](ClO_4)_2$ [1, 2].

Tetraamminecopper perchlorate $[Cu(NH_3)_4](ClO_4)_2$ (TACP) is one of the most interesting copper perchlorate-ammonia complexes. The preparation and fundamental physical and chemical properties of this compound were first described by Salvadori in 1911 [1] and later by Portillo in more detail [2, 3]. The fundamental explosive properties of this easily synthesized compound were described by several authors. Friederich and Vervoorst published that, unlike tetraamminecopper chlorate, TACP does not have initiating properties. The explosive strength of TACP measured using the Trauzl lead block test is between the strengths exhibited by primary explosives (like mercury fulminate and lead azide) and secondary explosives (like TNT or tetryl) [6]. Gorbunov and Shmagin measured the dependence of the burning rate of various tetraamminecopper complexes on pressure where TACP belongs among high-burning tetraammine complexes [7]. Explosive parameters of TACP (like detonation velocity, detonation pressure and heat of detonation) predicted by theoretical calculation were published as well [8]. Recently, Rećko *et. al.* measured the critical diameter and brisance for TACP phlegmatized with 5% paraffin wax. Based on their results, the critical diameter is 3 mm and brisance, according to Hess, is 91% TNT. The authors have even suggested phlegmatized TACP as a substitute explosive in time of conventional explosives shortages [9].

Due to a lack of experimentally determined explosive properties of pure TACP in the scientific literature, we decided to focus this study on the characterization of this complex potentially applicable as a burning rate modifier for propellants or as a blue flame coloring agent for pyrotechnics. Another aim of this paper is comparison of experimentally determined results with theoretical data obtained by the calculation using EXPLO5 code.

2 Experimental Section

Caution: Tetraamminecopper perchlorate is a sensitive explosive. Therefore it must be handled with care, and safety

[a] *O. Vodochodský, R. Matyáš, J. Kučera, J. Pachman*
Institute of Energetic Materials
University of Pardubice,
Faculty of Chemical Technology
Studentska 95, 53210,
Pardubice, Czech Republic
**e-mail: robert.matyas@upce.cz*
[b] *M. Künzel*
OZM Research s.r.o.
Blížňovice 32, 53862,
Hrochův Týnec, Czech Republic

precautions for handling explosives must be followed when working with TACP!!!

2.1 TACP Preparation

Tetraamminecopper perchlorate was prepared by the reaction of copper(II) perchlorate hexahydrate (98%, Acros Organics) with aqueous ammonia (24–29%, Penta). Copper perchlorate hexahydrate (100 g, 0.27 mol) was dissolved in aqueous ammonia (250 mL, 3.3 mol) while being stirred. The temperature was raised to 35 °C, the solution was allowed to cool slowly to ambient temperature and it was then cooled to 0 °C using an ice bath. The crystalized dark-blue product was filtered and left drying freely at room temperature. The yield was 77.0 g (86.5% of theory).

2.2 Analysis

Infrared spectra were collected using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) with an ATR single reflection diamond accessory GladiATR (Pike). Measurement parameters were the spectral region 4000–400 cm^{-1}, resolution 1 cm^{-1}, with 128 scans being performed. OMNIC 9.3 software was used for collection and processing of the spectra. FT-IR results for TACP (cm^{-1}): 3354 (ν_{as} NH_3), 3286 (ν_s NH_3), 3228 (ν NH_3), 3197 (ν NH_3), 1615 (δ NH_3), 1425, 1252, 1041 (ν_{as} ClO_4^-), 932 (ν_s ClO_4^-), 915, 685, 616, 459, 433.

Differential thermal analysis was performed using a DTA-551Ex differential thermal analyzer (OZM Research). Sample (30 mg) was heated at 5 °C min^{-1}. Meavy software was used for data collection and processing. DTA results for TACP: start of decomposition at 233 °C, explosion at 268 °C (literature: 236/270 °C [8], explosion within 20–30 seconds at 260 °C [6]).

Elemental analysis was performed on Vario MICRO Cube (Elementar) in CHNS mode with calibration on sulphanilamide, using a 1 mg sample for this analysis. Elemental analysis results for TACP: Calc. for $H_{12}N_4O_8CuCl_2$ (%): H 3.66, N 16.95. Found : C 0.1, H 3.58, N 16.22.

2.3 Sensitivity to Impact and Friction

Impact sensitivity was measured using a 2 kg Kast fall hammer, with BFH-SR guide rings and BFH-SC cylinders (OZM Research) being used for centering the sample. The sample volume was 40 mm^3. The Probit analysis method [10] was used for evaluation of the readings and to obtain the E_{50} value, and 5 energy levels were measured with at least 15 trials for each energy level.

Friction sensitivity was determined using a FSKM-08 BAM device with BFST-PT-100 S ceramic test plates and BFST–Pn-200 pestles (OZM Research). The sample volume was 10 mm^3. The Probit analysis method [10] was used for evaluation of the readings and to obtain the F_{50} value, with 6 friction force levels being measured with at least 15 trials for each force level.

Sensitivity curves for reference explosives mercury fulminate (MF), PETN and RDX were taken from our previous work [11].

2.4 Detonation Velocity Measurements

Detonation velocities of TACP have been measured by the fiber optic probe technique in aluminum tubes with wall thicknesses of 2 mm (diameters 4, 11, 16, 28 mm) and 0.5 mm (diameters 2, 3, 4, 6, 8 mm). The explosive was introduced into the tubes in small increments and tapped to a density of 0.90 ± 0.05 g cm^{-3}. For diameters 4 mm and higher, the VOD-815 tester (OZM Research) recorded arrival times of the detonation wave to the tips of 4 plastic fiber optic probes placed along the charge 40 mm apart. For charges with inner diameter 2 and 3 mm, the same arrangement was used with glass optical fibers and an OPTIMEX-64 passive optical system (OZM Research). The probes were introduced into the explosive through holes drilled in the casing and the probe tips were covered with aluminum tape to shield light preceding the reaction front. The first probe was positioned at a distance of at least five charge diameters from the booster charge of 5 g of Semtex 1 A plastic explosive (provided by Explosia a.s.) (Figure 1). The charges were initiated using RockStar industrial electric detonators (Austin Detonator). The detonation velocities have been determined as slopes using linear regression of the distance vs. time data.

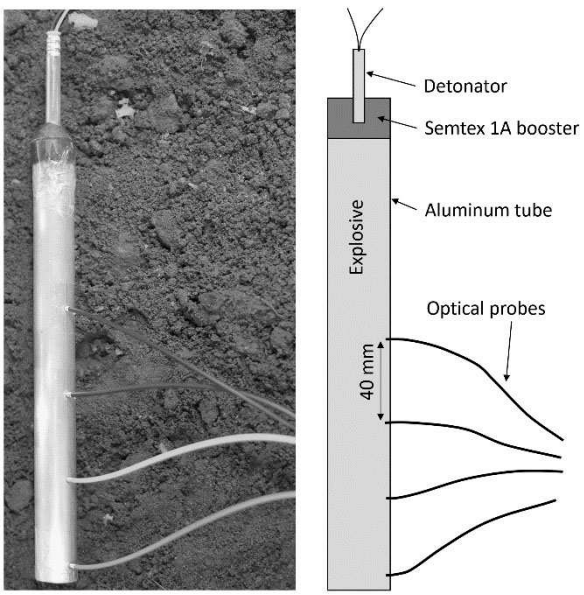

Figure 1. Charge for measurement of detonation velocity.

2.5 Cylinder Expansion Tests

Two reduced scale cylinder expansion tests have been performed to determine the Gurney velocity of powdered TACP. The tubes were made of un-annealed deoxidized high phosphorous copper. The tubes were 150 mm in length, 12.7 mm internal diameter and 1.27 mm nominal wall thickness. The actual wall thickness at the radial position corresponding to the probe location was used to determine the real metal to explosive mass ratio (*M/C*). The tubes were filled with TACP in small increments and tapped to a density of $0.91 \pm 0.01\ g\,cm^{-3}$. The charges were initiated using RockStar industrial electric detonators (Austin Detonator).

The expanding wall velocities were measured by a VeloreX PDV photonic Doppler velocimeter (OZM Research) combined with a DPO 70404 C oscilloscope (Tektronix) for signal acquisition. The cylinder was fixed in a 3D printed frame [12] with two PDV probes positioned 75 mm and 105 mm from the upper end of the tube (Figure 2). The probes' axes were angled 5° from the tube surface normal towards the detonator. The voltage-time oscilloscope readings were evaluated using short-time Fourier transform to obtain wall velocity vs. time profiles.

2.6 Calorimetry

The combustion experiments were carried out with BCA 500 closed bomb isoperibolic calorimeter (OZM Research). The 250 ml bomb containing 5 ml of water was flushed 3 times with pure oxygen gas (99.9%) at 2 MPa. The sample was placed at the bottom of a quartz crucible and combustion was initiated via electrical discharge through a iron alloy fuse wire approx. 6 cm long in contact with the sample. Four tests with benzoic acid pellets nominally weighting 1 g used for the instrument calibration resulted in the experimental heat capacity $\varepsilon COMB = 9301\ J\,K^{-1}$. Three experiments were carried out with TACP samples weighting 200–300 mg. The amount of released energy was determined from the corrected temperature increase.

The specific heat of detonation was measured using a DCA 25 isoperibolic detonation calorimeter (OZM Research). The calorimeter was calibrated by burning benzoic acid pellets in oxygen gas (99.995% O_2) at 2 MPa resulting in the calorimetric constant of $\varepsilon = 80.51 \pm 0.15\ kJ.K^{-1}$. Three tests were performed using powdered TACP samples confined in glass vials (Figure 3). Copper shell detonators with 1 g of PETN base charge were used for initiation. The previously determined heat of detonation of a single detonator was 6.4 kJ. Before the test, 20 ml of water were poured into the bomb to saturate the atmosphere with water vapor. The bomb was then closed, evacuated down to 1 kPa, and pressurized with nitrogen gas (99.95% N_2) to 2 MPa.

2.7 Thermochemical Calculations

The detonation parameters of TACP were calculated using the EXPLO5 V6.05.04 thermochemical code [13]. The Exp-6 fluid equation of state was used for the detonation products [14]. To be comparable with the experimental calorimetric results, the values of detonation heat were corrected for water condensation and HCl dissolution. The Gurney velocity was calculated using the recently published procedure using calculated isentropic expansion data [15]. The EXPLO5 code requires the enthalpy of formation as the calculation input. The only available H_f(TACP) value in the literature is $-661\ kJ\,mol^{-1}$ [7].

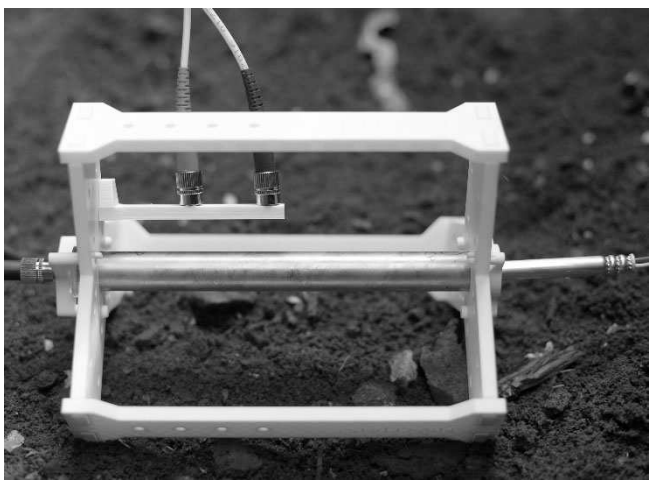

Figure 2. Charge for measurement of wall expansion.

Figure 3. Detonation heat measurement.

In our previous work we measured the heat of combustion to determine the enthalpy of formation of TACP. An erroneous assumption was made that the final composition of burning products equates to the equilibrium composition at the combustion temperature (CuO, N_2, H_2O and Cl_2) [8]. For this work, we measured the heat of combustion again (H_c(TACP) = 4315 kJ kg^{-1}) and re-evaluated the data considering equilibrium products at a temperature of 298 K (N_2, $CuCl_2$, H_2O and O_2) which better correspond to the final state in the combustion calorimeter. The resulting value of H_f(TACP) = −496 kJ mol^{-1} is used in this paper.

3 Results and Discussion

3.1 Sensitivity of TACP

Sensitivity of tetraamminecopper perchlorate was measured at various energy and force levels using Probit analysis. Impact energy with 50 % probability of initiation of the sample E_{50} was determined from the sensitivity curve obtained. The same procedure was used for friction sensitivity measurement and determination of friction force F_{50}. For both impact and friction, the observed positive reactions were clear decomposition of the sample. For impact sensitivity, the sample decomposition was mostly accompanied by a flash and strong acoustic effect. For friction sensitivity measurement, crackling was the most observed effect.

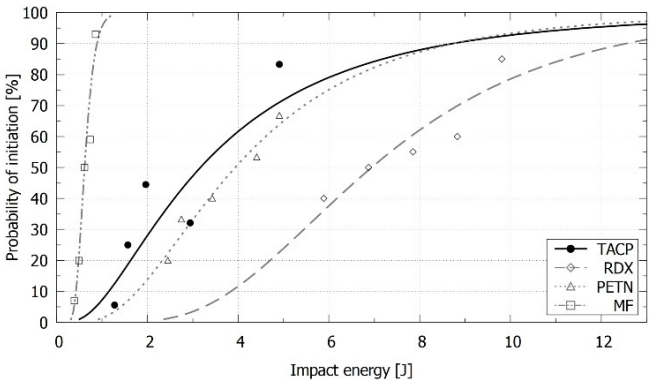

Figure 4. Impact sensitivity for TACP.

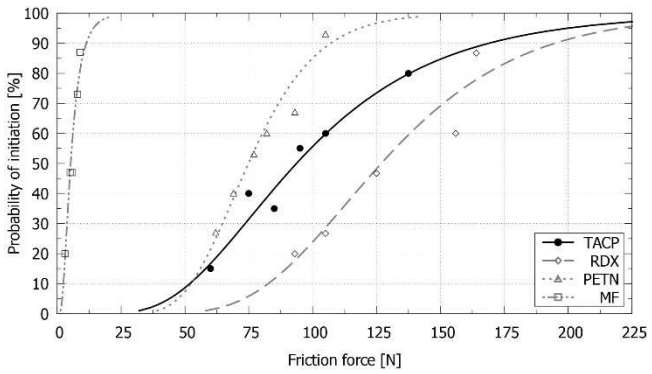

Figure 5. Friction sensitivity for TACP.

Results show that in terms of impact sensitivity, TACP is a highly sensitive explosive, slightly more sensitive than PETN, which is usually considered the border between primary and secondary explosives. Our E_{50} value corresponds well to the impact sensitivity recently published by Rećko *et al.* [9]. The whole impact sensitivity curve is shown in Figure 4.

The friction sensitivity curve for TACP is shown in Figure 5. Rećko *et al.* reported friction sensitivity of TACP of 130 N [9]. Our F_{50} value for TACP is between those for PETN and RDX. As can be seen from the probability curve, especially at the lower friction force, the probability of initiation is close to that of PETN and therefore in terms of safety it is appropriate and prudent to consider this explosive to be relatively sensitive.

The values of impact energy E_{50} and friction force F_{50} for TACP as well as for the reference explosives are shown in Table 1.

3.2 Detonation Velocity

Two series of detonation velocity measurements have been carried out with charges confined in aluminum tubes with 0.5 mm and 2 mm wall thicknesses. The infinite diameter detonation velocity was found by extrapolation of the measured data (Figure 6). Although the experimental points are quite scattered, possibly caused by local density variations, the extrapolated velocities from the two series almost match each other. They also match the detonation velocities measured in the cylinder tests and the values calculated by the EXPLO5. The infinite diameter detonation velocity of TACP is slightly lower compared to the previously published data on tetraamminecopper nitrate (TACN) at the same density [16] but it is much less diameter dependent. For 2 mm wall thickness, the measured detonation velocities were 3130 m s^{-1} and 2900 m s^{-1} in the 28 mm and 4 mm diameter aluminum tubes, respectively. Even in a weak confinement of 0.5 mm aluminum wall and charge diameter as small as 2 mm, the TACP fully detonated with the velocity of 2330 m s^{-1}. The critical diameter of TACP is there-

Table 1. Sensitivity of TACP.

Explosive	Impact sensitivity E_{50} [J]	Friction sensitivity F_{50} [N]
MF [a]	0.62	5.3
PETN [a]	3.9	75
RDX [a]	7.0	127
TACP	2.6	93

[a] E_{50} and F_{50} values were taken from [11].

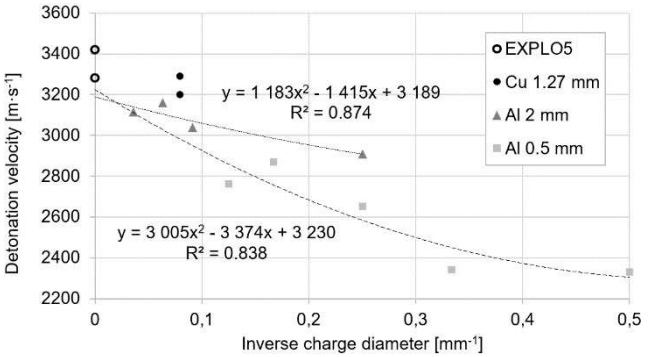

Figure 6. Detonation velocity dependence on the inverse charge diameter for charges with various confinement options compared to the EXPLO5 prediction.

Table 2. Summary of the measured and calculated detonation parameters of TACP at 0.9 g cm^{-3}. D = detonation velocity (extrapolated value for infinite diameter), G = Gurney velocity, H_d = Heat of detonation.

Parameter	Experiment	EXPLO5[a]	EXPLO5[b]
D [m.s^{-1}]	3228 ± 40	3281 (+1.6%)	3419 (+5.9%)
G (V/V_0 = 7) [m.s^{-1}]	1536 ± 29	1449 (−5.6%)	1541 (+0.3%)
H_d (H_2O(l)) [kJ.kg^{-1}]	4322 ± 83	3748 (−18.9%)	4241 (-1.9%)

[a] using literature value H_f(TACP) = −616 kJ mol^{-1} (1865 kJ kg^{-1}) [7]. [b] using our value H_f(TACP) = −496 kJ mol^{-1} (1502 kJ kg^{-1}).

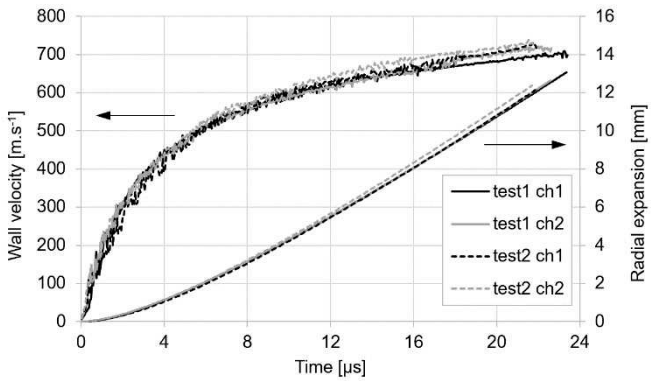

Figure 7. Wall velocity and radial expansion profiles from the small scale cylinder expansion tests.

fore lower than 2 mm. The infinite diameter detonation velocity of TACP at 0.9 g cm^{-3} is shown in Table 2.

3.3 Cylinder Tests

The wall velocity profiles obtained from the reduced scale cylinder expansion tests are almost identical within the first 3 mm of radial expansion but slightly diverge later on, which corresponds to some degree of inhomogeneity of the charge (Figure 7). The standard deviations of both wall velocity and Gurney velocity values at V/V_0 = 7 are 1.8%. The result is in a good agreement with the values predicted by the EXPLO5 code (Table 2). The relative Gurney velocity of TACP is 66% of the PETN value (2320 m s^{-1} at 0.9 g cm^{-3}) [17].

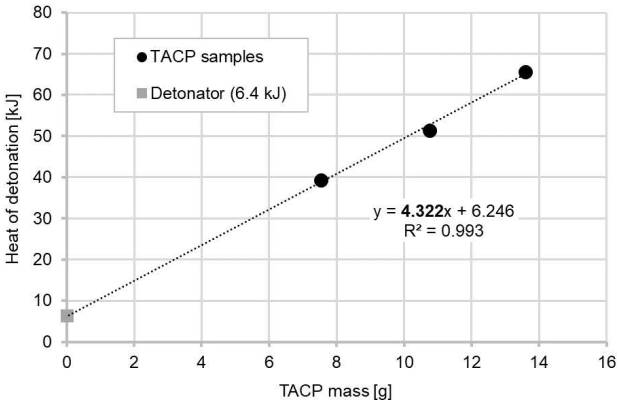

Figure 8. Heat of detonation of TACP is detemined as a slope of the regression line. The intercept matches with the heat produced by the detonator.

3.4 Heat of Detonation

The specific heat of detonation was determined by linear regression of the heat-mass dependence from 3 shots with different sample mass. The slope of the regression line reveals the value of H_d(TACP) = 4322 kJ kg^{-1}. The intercept with the y axis corresponds to the heat produced by the detonator although the detonator value was omitted from the regression (Figure 8).

From Table 2, it can be seen that the measured heat of detonation is in good agreement with the EXPLO5 result calculated using our value of H_f(TACP).

4 Conclusion

Sensitivity and detonation parameters of tetraamminecopper perchlorate were measured. TACP is a highly sensitive explosive, slightly more sensitive to impact than PETN. Friction sensitivity for TACP is between those for PETN and RDX. The infinite diameter detonation velocity of TACP at a density of 0.9 g cm^{-3} was found to be 3230 m s^{-1}. Measurements have also shown that the critical diameter of TACP is less than 2 mm. Heat of detonation determined by detonation calorimetry is 4322 kJ kg^{-1}. Measured values of detonation parameters correspond to the values calculated by the EXPLO5 code using the updated heat of formation of −496 kJ mol^{-1}.

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