



THERMOLYSIS AND THEIR KINETICS OF Cu(II) PERCHLORATE COMPLEX WITH ISOPROPYLAMINE AND WATER

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Abstract

Copper perchlorate complex containing isopropylamine (ipa) has been prepared with the molecular formula $[\text{Cu}(\text{ipa})_3(\text{H}_2\text{O})(\text{ClO}_4)]\text{ClO}_4$. It was characterised by elemental analysis, IR spectroscopy and thermogravimetric data. Response of the complex to heat has been studied by thermogravimetry (TG) in static air and simultaneous thermogravimetry-derivative thermogravimetry-differential thermal analysis (TG-DTG-DTA) in flowing nitrogen atmospheres. The complex decomposes in three steps, although the resolution between the steps is less. Possible decomposition pathways have been proposed for decomposition in static air and flowing nitrogen atmosphere. Thermolysis kinetics have also been investigated using isothermal TG data recorded at five different temperatures and applying model-fitting and isoconversional methods. An application of model-fitting methods has yielded a single activation energy value, whereas an isoconversional method has yielded a series of activation energy values for each extent of conversion, α . Differences in decomposition patterns under air and inert atmosphere have been also discussed.

Keywords: Isopropyl amine, perchlorate, complex, thermolysis, kinetics.

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1.0 INTRODUCTION

Perchlorate (ClO_4^-) is readily formed by various atmospheric processes and it may have their presence in rain water or even in ice [1] and it may have their availability in ground water also [2]. Perchlorates have been detected in ice covered lakes in the dry valleys of Antarctica [3]. Analysis of soil of Mars from Phoenix landing site have identified perchlorates using wet chemistry laboratory on Phoenix [4, 5]. Isopropylamine (ipa), a neutral monodentate ligand when complexes with metal ions having ClO_4^- as a counter anion, the complex undergoes self-propagative decomposition reactions due to the presence of both oxidizing (ClO_4) and reducing (ipa) groups in the same molecule [6, 7]. Several investigations are reported on thermal decomposition studies of energetic metal amine complexes [8–11]. High energy parameters of these types of complexes lie between those of primary and secondary explosives [11]. These types of complexes are found to act as burn rate enhancers for solid propellants [12–16]. At the end of decomposition these complexes leave out respective metal oxide/oxides which can be used in anodic material for lithium-ion batteries [17], photo inorganic electrochromic films [18], gas sensors, self-cleaning and photocatalysis [19] and composite solid propellants as burning rate modifiers [20,21]. 3d metal(II) perchlorate complexes based on 1-amino-5-methyltetrazole were found to have thermal stabilities up to 199 °C and characteristics of primary explosives [22]. Energetic properties of copper(II) perchlorate complex with aminoguanidine have been investigated by Mohammad Mahdavi et al. [23]. Cytotoxicity of perchlorate complexes of Zn(II) and Cu(II) with nicotinamide; $[\text{Zn}(\text{Nia})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ and $[\text{Cu}(\text{Nia})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (Nia = Nicotinamide,

niacinamide, 3-pyridinecarboxamide, $\text{C}_5\text{H}_4\text{NC}(\text{O})\text{NH}_2$) have been reported by N. S. Rukk et al. [24]. Owing to the interest and various applications of metal amine perchlorate complexes, we present here the preparation, characterisation and thermolysis of copper perchlorate complex with iso-propyl amine, water, and ClO_4^- as ligands. Kinetics of thermolysis (upto 30% mass loss) will be also investigated by applying model-fitting as well as isoconversional methods.

2.0 EXPERIMENTATION

2.1 Materials

Cupric carbonate, perchloric acid, iso-propyl amine (s.d. fine), ethanol (ChangshuYangyuan Chemical, China), petroleum ether (Merk), all of AR grade were used as received.

2.2 Preparation

The complex was prepared via a two-step procedure. In the first step, hexahydrate cupric perchlorate was obtained by reacting cupric carbonate with 60% perchloric acid followed by recrystallisation. In the second step, an ethanolic solution of cupric perchlorate hexahydrate and iso-propyl amine in 1:3 molar ratios was mixed together and stirred well at room temperature. Some blue precipitate appeared which were filtered out. From the filtrate, after 4-5 days blue shining crystals started to appear. The crystals were separated, washed with alcohol and dried.

2.3 Characterisation

Complex was characterised by elemental analysis (C, H, N; Thermo Finnigan Flash EA 1112 CHNS analyzer), infrared [25–27] (Perkin Elmer FT-IR spectrometer), and thermogravimetry [28] (Table 1). Tentative structure of the complex is presented in Fig. 1 and 2.

Table 1: IR frequencies and elemental analysis data for the complex

IR		Element/%, Observed/calculated	
v/cm ⁻¹	Assignments		
395, 427, 466	M-N, M-O	C	24.18/23.61
1089	Ionic perchlorate	N	9.18/9.18
1112, 1145	Bidentate ClO_4	H	5.99/6.33
1220	C-N str.		
1298, 1251	C-O str.		
1396, 1380	C-H def.		
1587, 1603	N-H bend.		
2974, 2941	C-H str.		
3311, 3261	NH ₂ (Pri)		
3452 (broad)	O-H str. (H ₂ O)		

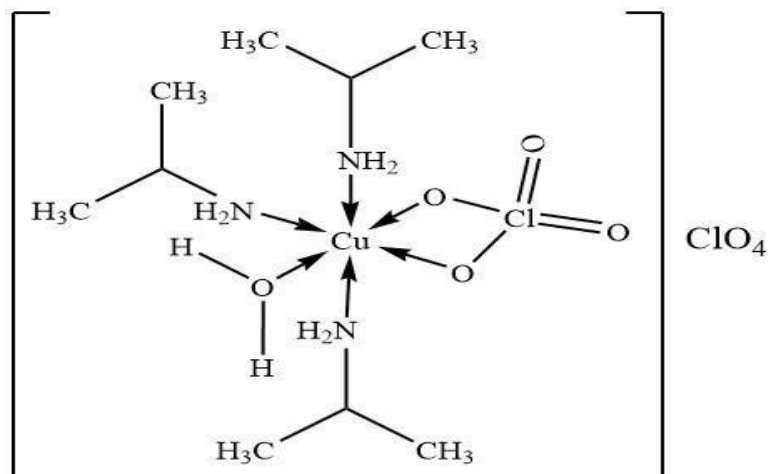


Fig. 1 Tentative structure of the complex

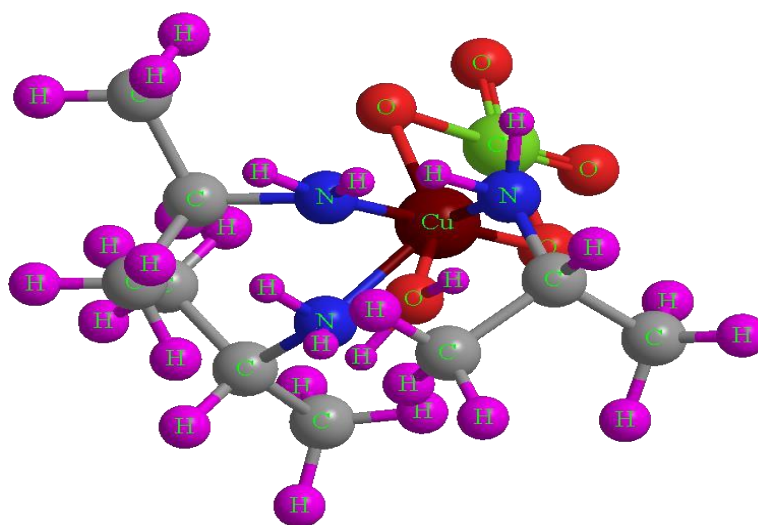


Fig. 2 Tentative 3D structure of the complex

2.4 Thermal Analysis

TG (Fig. 3) was recorded at 10°C/min (mass 20 mg) using an indigenously fabricated TG apparatus [29]. Simultaneous TG-DTG-DTA traces of the complex were obtained in a flowing nitrogen atmosphere (100 ml/min) using sample

mass 1.715 mg at a heating rate of 10°C/min (Fig. 4, Table 2). Isothermal TG (Fig. 5) has been recorded in static air using the above-mentioned indigenously fabricated TG apparatus at five different temperatures (160, 170, 180, 190 and 200 °C).

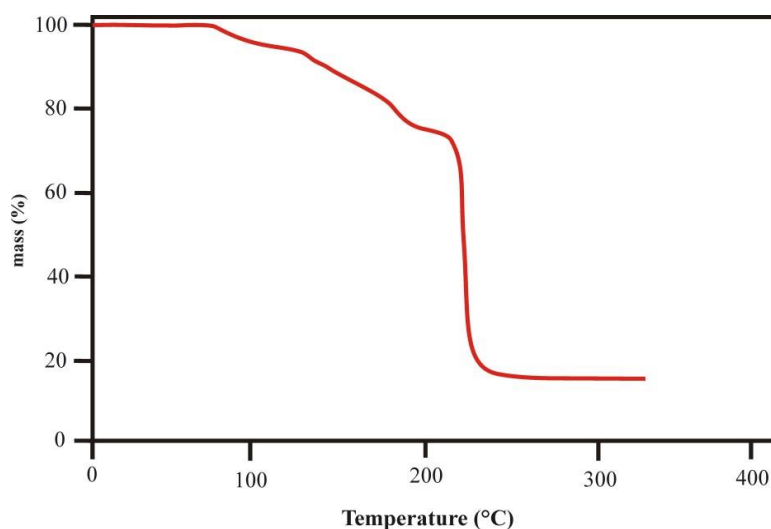


Fig. 3 TG curve of the complex in static air atmosphere

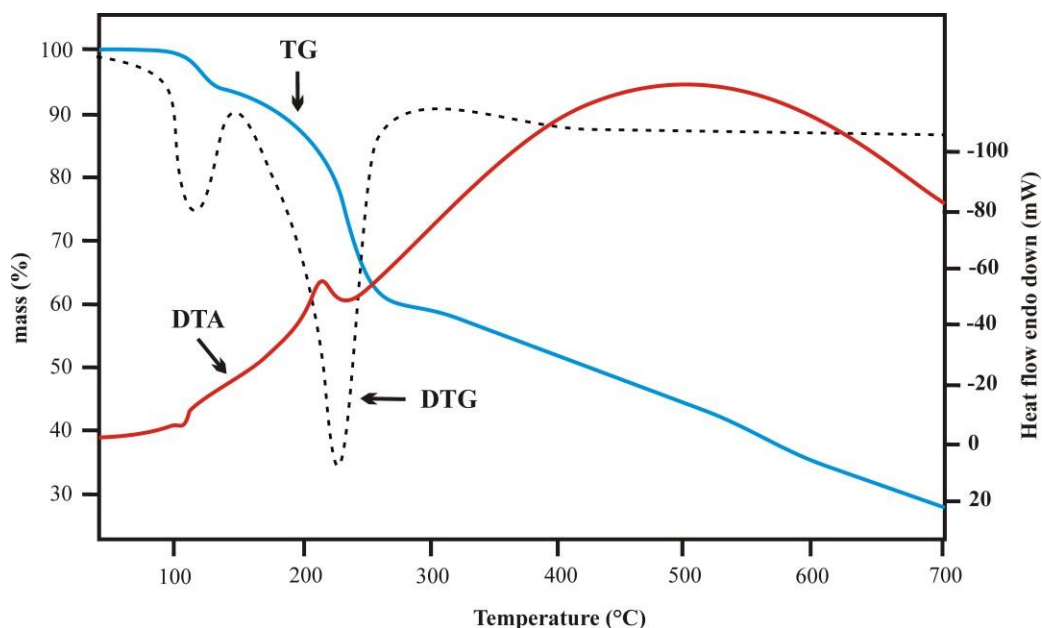


Fig. 4 TG-DTA curve of the complex in flowing N₂ atmosphere

Table 2: TG-DTA data of the complex in flowing nitrogen atmosphere

TG (Static air)			TG (Flowing N ₂)			DSC (Flowing N ₂)	
Step	Temperature range/°C	% Decomposition ~Observed/Calculated	Step	Temperature range/°C	% Decomposition ~Observed/Calculated	Peak position/°C	Nature of peaks
I	88-103	4.0/3.98 (-H ₂ O)	I	90-100	4.0/3.98 (-H ₂ O)	120	Endo
II	103-218	24.0/25.78 (-2ipa)	II	124-262	34.6/38.7 (-3ipa)	225	Endo
III	218-225	54.0	III	262-716	34.5	--	Broad hump exo

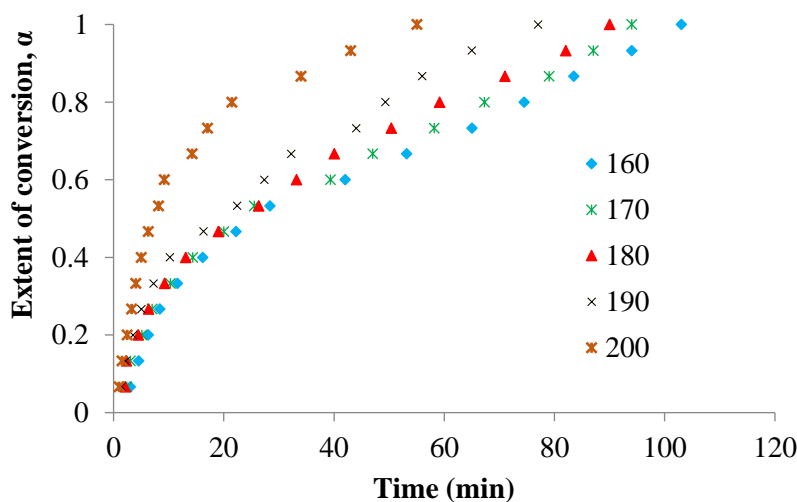


Fig. 5 Isothermal TG of the complex in static air atmosphere at different temperatures

2.5 Kinetic Analysis

Kinetics of thermal decomposition has been explored by recording isothermal TG data using model fitting (Table 3) [30] and isoconversional

methods [31, 32]. Variation in activation energy value with extent of conversion, α is given in Fig. 6

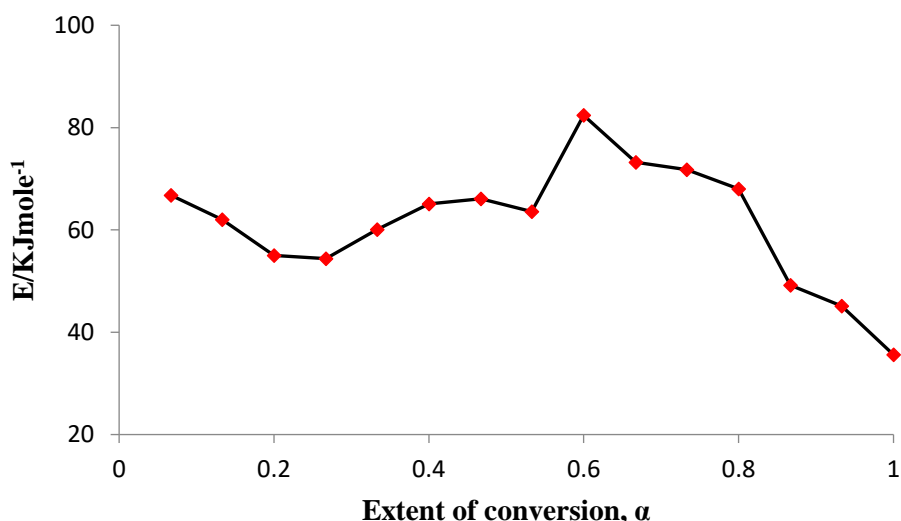


Fig. 6 Variation of activation energy of thermolysis for the complex with extent of conversion, α

Table 3: Activation energy (E_a), Arrhenius factor and correlation coefficients (r) for the isothermal decomposition of the complex

S.No.	Model [Integral form]	E (kJ/mol)	r	Mean dev	Stddev
1	Power law [$\alpha^{1/4}$]	25.1	0.9493	2.684	2.834
2	Power law [$\alpha^{2/3}$]	25.3	0.9484	2.576	2.720
3	Power law [$\alpha^{1/2}$]	25.7	0.9465	2.442	2.580
4	Power law [$\alpha^{3/2}$]	27.9	0.9362	2.225	2.352
5	Parabolic law [α^2]	28.8	0.9321	2.210	2.338
6	Mampel [$-\ln(1-\alpha)$]	36.5	0.9126	1.714	1.823
7	Avrami-Erofeev [$-\ln(1-\alpha)^{1/4}$]	24.9	0.7652	2.331	2.465
8	Avrami-Erofeev [$-\ln(1-\alpha)^{1/3}$]	25.3	0.9484	2.576	2.720
9	Avrami-Erofeev [$-\ln(1-\alpha)^{1/2}$]	25.7	0.9465	2.442	2.580
10	Contracting sphere [$1(1-\alpha)^{1/3}$]	17.7	0.9685	2.395	2.527
11	Three-dimensional diffusion	36.3	0.9173	2.431	2.574
12	Contracting cylinder [$1(1-\alpha)^{1/2}$]	30.0	0.9305	2.306	2.439
13	Prout-Tompkins [$\ln(\alpha/1-\alpha)$]	34.4	0.9223	1.413	1.507
14	Ginstling-Brounshtein	32.4	0.9230	2.849	3.011

3.0 RESULTS AND DISCUSSION

Elemental data presented in Table 1 ensure a satisfactory agreement between observed and calculated mass percents of C, H and N. FT-IR frequencies at 395, 427, 466 have been assigned to (M–N), (M–OH₂) and (M–OCIO₃) respectively. Peaks at 1112, 1145 are characteristics of bidentate perchlorate (C_{2v} symmetry). Peak at 1089 cm⁻¹ has appeared for ionic perchlorate. A broad peak at 3452 cm⁻¹ is due to (O–H) of coordinated water. Other reported IR frequencies are according to the standard literature. In light of the above discussion, the molecular formula of the complex can be given as [Cu(ipa)₃(H₂O)(ClO₄)]ClO₄ in which Cu²⁺ is hexacoordinated. Out of six coordination sites, three sites are satisfied by the N atom of three isopropylamines, two sites are occupied by one ClO₄⁻ ion acting as a bidentate ligand, and one site is satisfied by the O atom of the H₂O molecule (Fig. 1 and 2).

The thermogravimetric curve recorded in static air with a linear increase in temperature (Fig 3) shows that the complex decomposes in three steps (Table 2). First step (88–103°C) is gradual where coordinated H₂O leaves the complex (~4% wt. loss, calc. 3.98%). In the second step (103–218°C) about 24% mass was released out which corresponds to the two isopropyl amine moiety (calc. mass 25.78%). In the third step (218–225°C) the remaining residue [Cu(ipa)(ClO₄)]ClO₄ undergoes exothermic redox reactions (ignition) and give a sharp mass loss of ~54%. At the end ~16% mass is left which corresponds to CuO (calculated mass 17.4%). The residue left is slightly less than 17.4% because some of the content has fallen down from the open crucible during ignition.

In flowing nitrogen atmosphere (Fig. 4, Table 2) the decomposition pattern of complex differ to that in static air except step first (90-100°C) where a water molecule is lost. An endothermic

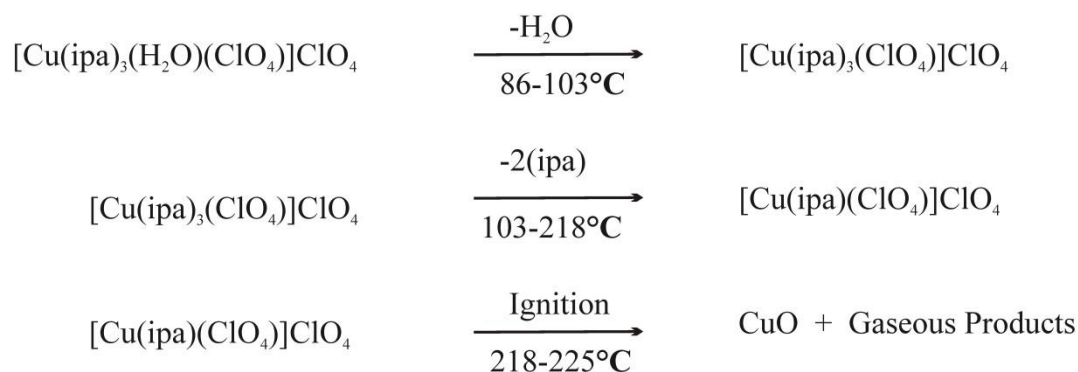
peak at 120°C in DTA trace has been appeared for this step of water loss. In second steps ~35% mass loss has appeared which may be attributed to loss of one of the molecule of isopropyl amine and a coordinated perchlorate anion ((calc. mass 34.59%) giving a sharp mass loss in TG curve. Perchlorate (oxidiser) and isopropyl amine (fuel) have gone through exothermic redox changes and an exothermic peak at 225°C has appeared in the DTA curve. The remaining residue, [Cu(ipa)₂]ClO₄ decomposes exothermically at a slow rate over a wide range of temperatures giving the third step of gradual mass loss. This step of weight loss is very slow because there are not sufficient oxygen atoms (negative oxygen balance) to combust the remaining two isopropyl

amine molecules. A broad exotherm has appeared for this step. Two DTG peaks have been obtained corresponding to the first and second steps of weight loss. DTG peak was not obtained for third step because this step is very gradual.

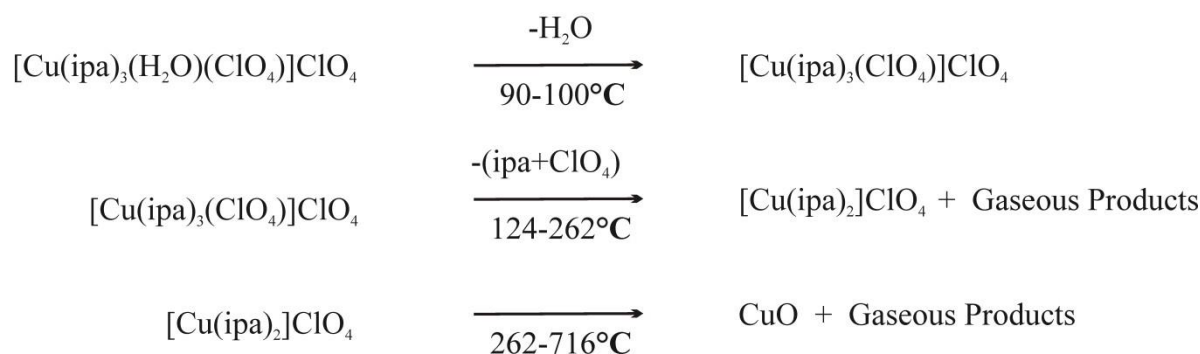
Thermolysis of the complex in static air is fast as compared to nitrogen atmosphere. The complex has decomposed to CuO up to 250°C in air whereas in inert atmosphere it requires a very high temperature up to 700°C. The difference in the thermolytic pattern of the complex in air and in inert atmosphere is due to the oxidative nature of the air.

Thus, the above discussion can be summarised by the thermal decomposition pattern of the complex as given below:

Thermolytic pattern of the complex in static air



Thermolytic pattern of the complex in flowing N₂



A set of reaction models (Table 3) [30] was applied to isothermal TG data recorded at 160, 170, 180, 190 and 200°C (Figure 3) in the order to investigate the activation energy (E_a) for the removal of one H₂O and two isopropyl amine ligands (30% wt. loss, calc. mass 29.71%). E_a values obtained varies from 17.7 to 36.5 kJ/mol depending upon the model applied. A single value of activation energy is not sufficient to explain such a complex state thermal decomposition. In contrast to model-fitting methods when

isoconversional method [29, 30] is applied for kinetic analysis of isothermal TG data, it results in a series of activation energy values corresponding to the extent of conversion, α (Fig. 6). Thus, the model-free isoconversional method yields a better solution to investigate consistent and reliable thermokinetic data as compared to the model-fitting methods.

4.0 CONCLUSION

The complex $[\text{Cu}(\text{ipa})_3(\text{H}_2\text{O})(\text{ClO}_4)]\text{ClO}_4$ was prepared and characterised by various techniques. Analysis of TG-DTA traces have shown that the complex decomposes in three steps either in air or in inert atmosphere although pattern of thermolysis differ. In air atmosphere decomposition completed upto 250°C but in flowing nitrogen it completes upto 700°C . An endothermic, an exothermic peak and a broad exothermic hump have appeared in the DTA curve. End product of thermolysis corresponds to CuO. Activation energy for 30% weight loss has been found to vary with the extent of conversion, α .

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