

ROLE OF ADDITIVES IN THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE AND EVIDENCE SUPPORTING THE IDENTIFICATION OF NITRYL PERCHLORATE AS THE ESSENTIAL REACTION INTERMEDIATE

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ABSTRACT

NO_2ClO_4 was identified as the essential reaction intermediate in a recent study of the thermal decomposition of ammonium perchlorate (AP) (A.K. Galwey and M.A. Mohamed, *Proc. R. Soc. London, Ser. A*, 396 (1984) 425). Here, we report further measurements of the influences of selected additives on the same reaction; all the observations are consistent with, and provide support for, the earlier mechanistic conclusion.

Attempts to introduce synthetic NO_2ClO_4 directly on to the AP reactant resulted in no marked acceleration of reaction, an observation readily explained by the instability of the additive at reaction temperature (ca. 5 s lifetime) and its sensitivity to hydrolysis. In addition, the reaction rate of AP prepared with a low water content was greater than that of salt recrystallized from water, which can be explained by a lessening of the extent of hydrolysis of NO_2ClO_4 . The effects of finely divided platinum metal and of lattice-incorporated CrO_4^{2-} in promoting AP decomposition are identified with the abilities of these additives to oxidize ammonia. Lattice-incorporated sulphate and phosphate ions exhibited little or no influence on the AP decomposition rate.

INTRODUCTION

In a recent article [1] on the thermal decomposition process in ammonium perchlorate (AP), it was concluded that the essential reaction intermediate was nitryl perchlorate. This mechanism was based on new microscopic, kinetic and analytical data and resolved evident shortcomings in the accepted alternative reaction models [2–4] in which the rate-controlling step was

identified as either proton transfer or electron transfer. The important characteristic of this new intermediate is that the stability of the perchlorate ion (which determines the reaction rate) is reduced by forming a covalent bond, $O_2N-O-ClO_3$. The thermal stability of such covalently-bonded perchlorates is significantly less than that of the alkali metal (ionic) perchlorates, for example, which contain the ClO_4^- ion [5]. Nitryl perchlorate decomposes at a lower temperature than AP [3,6].

Quantitative kinetic comparisons showed that the AP reaction rate agreed with expectation for a process controlled by the small amount (ca. 0.08%) of NO_2ClO_4 determined analytically to be present in partially decomposed AP. The rate-determining step is regarded [1] as being the same as that controlling breakdown of the intermediate, probably rupture of the $O_2NO-ClO_3$ bond. The intermediate, together with subliming reactant and other products (H_2O , $HClO_4$, oxides of nitrogen, etc.) are contained in fluid droplets located at the closed extremities of an advancing pore system that constitutes the active reaction interface. At this interface ammonia oxidation leads to regeneration of the essential intermediate (NO_2ClO_4) and this perpetuates the process. Each hollow pore is the track of an advancing, chemically highly reactive droplet within which, or at the surface of which, AP decomposes. Compositional analysis of the very small volumes of this highly unstable mixture is impracticable.

The ability of oxidized nitrogen species to promote AP decomposition was recognized from the observation that nitrates reduced the induction periods and accelerated the reaction. The magnitude of this effect varied with the cation present [1,7]. Small, but significant amounts of oxidized nitrogen were detected [1] analytically in specimens of pure AP which had been partially decomposed in the absence of all additives. The only compound that could be realistically envisaged [1] as being capable of transitory existence at AP reaction temperatures is NO_2ClO_4 and, as already pointed out, its thermal stability is in quantitative agreement with expectation for its participation as an intermediate.

This model, in which reaction occurs within discrete fluid-foam droplets that individually penetrate the unreacted crystal, explains the unique features of the reaction. In powders, pellets and millimetre-sized crystals, decomposition yields a porous, channelled product, leaving an unreacted residue comprising about 70% of the original reactant weight [2-4,8]. This participation of a fluid phase is consistent with recent mechanistic explanations of chemical changes involving solid reactants: e.g. alum dehydrations [9], $(NH_4)_2Cr_2O_7$ decomposition [10], and the $KBr + Cl_2$ reaction [11].

We have recently investigated [12] the textural changes of the AP surface during the initiation and establishment of decomposition growth nuclei. Optical microscopic examinations showed that during, or immediately following, heating a pattern of circular features was generated. This appeared [13] to be due to surface tension control, rather than crystallographic lattice

forces, and is identified as surface bubble formation. This transient phenomenon is envisaged as involving a viscous liquid/gas mixture composed of perchloric acid and volatile products on the surface in which water is an essential component. Subsequently sublimation, with concurrent surface migrations, developed grooves on the crystal face in which holes later appeared. This progressive retexturing is regarded as a consequence of the autocatalytic character of the reaction, whereby the products promote AP decomposition. Such local enhancement of chemical change culminates in penetration of the crystal bulk along the dislocation lines, or their strain fields, through the appearance of the active fluid droplets containing the intermediate and associated species. Replication techniques [14] enabled information to be obtained about the labyrinthine distribution of these pores. Each progressed in a torturous manner, consisting of short linear, crystallographically oriented sections and each included void volumes indicating regions of enhanced reactivity. The evidence also confirmed the branching of such pores, the local development of intranuclear holes and the continuous and interlinked nature of the pore structure within each decomposed zone.

This paper extends our previous investigations [1,7,12] by considering the effects of further selected additives on AP decomposition, including sulphuric and phosphoric acids and the chromate ion, CrO_4^{2-} . These observations are discussed in the context of the recently proposed mechanism [1]. We have also attempted to introduce NO_2ClO_4 directly on to the reactant surface of AP. It must be emphasized, however, that the marked instability [3,6] of this substance at reaction temperature (the property that accounts for its participation in AP decomposition) makes it unlikely that this experiment can be performed satisfactorily.

EXPERIMENTAL

Apparatus

The apparatus and experimental methods were identical with those described previously [1]. Kinetic measurements were always made under isothermal conditions (± 0.7 K) from the pressure of permanent gases evolved in the constant volume apparatus: a 78 K trap was maintained between reactant and gauge. The present kinetic investigations were undertaken concurrently with the microscopic studies which will be reported elsewhere [12].

AP reactant

The reactant was the same as that used in previous work [1,7,12]. Large crystals, with well-defined habit were prepared by slow recrystallization

from aqueous solution. Various reactant pretreatments are described at the appropriate places in the text below.

RESULTS AND DISCUSSION

Nitryl perchlorate and AP

The most reliable method of investigating the role of a postulated reaction intermediate is to monitor the consequences of introducing a known, appropriate quantity of that substance into the reactant. Its participation will then be confirmed if the reaction rate is enhanced as predicted from consideration of the amount present during reaction of the pure compound. Here, direct introduction of the intermediate would be expected to reduce markedly, perhaps even eliminate, the induction period.

Mindful of the extreme sensitivity of NO_2ClO_4 to hydrolysis [3], together with its instability at temperatures $> 500 \text{ K}$ [6], we used several variations of experimental technique in attempts to determine the effects of this additive. The most meaningful and reliable observations are summarized in Fig. 1.

NO_2ClO_4 was prepared [3] by boiling 1 : 1 mixtures of pure, anhydrous HClO_4 and HNO_3 . With minimum delay and under dry conditions this was

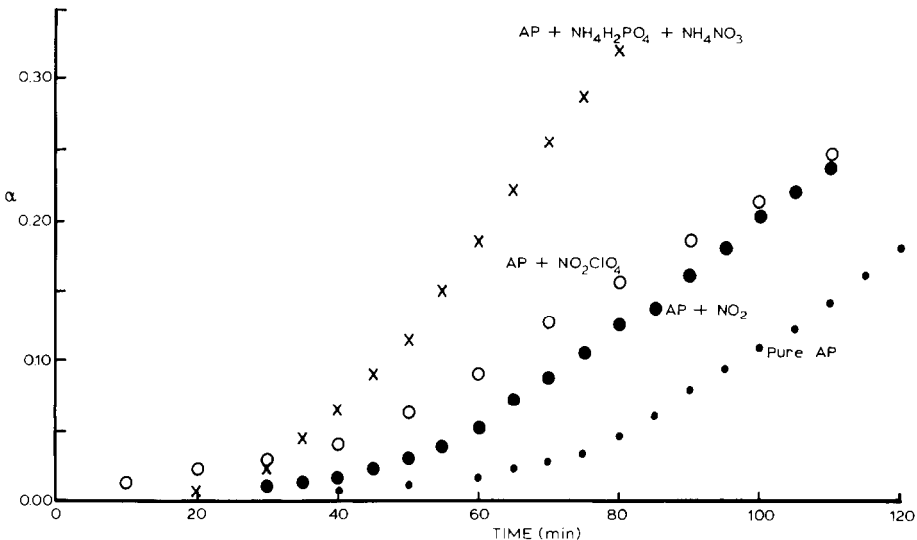


Fig. 1. Fractional reaction α vs. time curves for the isothermal decomposition at $508 \pm 1 \text{ K}$ of pure AP (●) and AP to which the following compounds have been added: NO_2 liquid (●), NO_2ClO_4 (○) and an $\text{NH}_4\text{NO}_3/\text{NH}_4\text{H}_2\text{PO}_4$ mixture (×), (for detailed explanation of behaviour see text). It is concluded that NO_2 and NO_2ClO_4 are rapidly volatilized and/or hydrolyzed so that the effects are small. Oxidized nitrogen retained in the molten phosphate phase was the most effective of these additives in initiating reaction.

directly placed on reactant AP crystals. After rapid outgassing, the kinetics of decomposition were studied under the usual conditions (see Fig. 1). The induction period was somewhat reduced by the additive, but the decomposition rate was not appreciably increased. The effect was less than anticipated and closer to that which would be expected [15] from the addition of HClO_4 to AP. It should be recalled, however, that NO_2ClO_4 would be decomposed in less than 5 s at 509 K [6]. Involvement of the intermediate in the continued reaction requires the specialized intracrystalline pore system and foam within which its regeneration is effective [1]. When NO_2ClO_4 is placed on an external flat AP face very rapid hydrolysis by surface [12], constituent [1], or product [15] water is expected. Thus directly added NO_2ClO_4 cannot survive sufficiently long to generate the structure capable of propagating AP decomposition.

Nitric oxide and AP

The influence of NO_2 on AP decomposition, added either as a gas or as a liquid, is shown in Fig. 1. Again, the resulting behaviour observed is ascribed to volatilization of the additive before nucleus development.

$\text{NH}_4\text{NO}_3/\text{NH}_4\text{H}_2\text{PO}_4$ and AP

This mixture was the most effective of all the additives studied both in reducing the induction period and in accelerating subsequent decomposition (Fig. 1). We ascribe this to the effective retention of oxidized nitrogen at the crystal face of the AP crystal. The accelerated reaction is similar to that previously described [1] for NH_4NO_3 addition.

Influences of other additives

Platinum metal and AP

On crushing AP in a pestle and mortar with platinum metal (10% by weight, finely divided platinum black) the induction period was reduced from ca. 50 to ca. 15 min at 503 K and the maximum rate of the subsequent decomposition was increased ca. 1.4 times. The added metal did not increase the yield of permanent gas products. While the detailed reaction mechanism is not elucidated here, we believe that this activity is due to the well-known ability of platinum to catalyze the oxidation of ammonia. Initial locally enhanced reactivity on the metal particles may also enhance surface retexturing with pit formation thus increasing both rate and density of nucleation. This is consistent with the previously described reaction mechanism [1].

Sulphate and phosphate ions

Several articles [2,3,16,17] have discussed the roles of cation and anion additives of different valency on AP decomposition kinetics, often with

reference to the participation of lattice vacancies in the reaction. Accordingly, a number of comparative rate measurements were made for reactions of single crystals of AP at 503 K in which sulphate or phosphate was present, as described below.

Doping. Large AP crystals of well-defined habit were grown by slow evaporation of aqueous AP solutions containing $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{SO}_4$: the crystals retained 1–3% molar additive. On subsequent decomposition of these doped reactant crystals there was no detectable change in the length of the induction period or in the initial rate of the acceleratory reaction. The later part of decomposition was just detectably less deceleratory than for pure AP crystals but the effect was small, comparable with the variations in rate between individual single crystals. This result differs from the behaviour found [4,17] from a variety of other lattice-incorporated additives.

Crystals. During vacuum reactions, $(\text{NH}_4)_2\text{SO}_4$ crystals sublimed relatively rapidly and the transitory initial presence of such a crystal exerted no detectable influence on the decomposition of an AP crystal with which it had been in contact.

$\text{NH}_4\text{H}_2\text{PO}_4$ was of greater interest because it melts at 463 K, and therefore could provide a liquid medium for AP breakdown, if it is soluble. This relaxation of lattice stabilizing forces was expected [18] to enable reaction to proceed more rapidly than in the crystalline state. However, no perceptible changes in the kinetics of AP decomposition resulted.

This is consistent with previous observations [19] for the $\text{LiClO}_4\text{--NH}_4\text{ClO}_4$ system where it was shown that AP was significantly more stable in a liquid eutectic at 473 K than in the solid state. Decomposition of crystalline AP is, therefore, a consequence of the specific chemical changes proceeding on the reactant surface or within the pore structure. In the absence of conditions enabling the autocatalytic behaviour to propagate, the perchlorate is stable [5] at 473 K, even in the liquid state.

Acids. Added sulphuric or phosphoric acid on reactant surfaces could be expected to dissolve superficial species, including intermediates, and thus influence the subsequent reaction. The addition of ca. 50 mg of either H_2SO_4 or H_3PO_4 to a single AP crystal of equal weight resulted in a small (ca. 20%) increase in the induction period to reaction at 506 K and a small reduction in the rate of subsequent AP decomposition. This behaviour is attributed to some dilution of surface species by the inert acid medium and is consistent with the proposed mechanism [1]. The observation, however, contrasts markedly with the well-known ability [2,3,15] of HClO_4 to promote the onset of reaction. We conclude, therefore, that the role of HClO_4 is not proton donation (because the strong acids H_2SO_4 and H_3PO_4 are ineffectual) and the ability to promote reaction is associated with the participation of oxidized chlorine. The influence of the readily volatilized nitric acid (HNO_3 boils at 356 K) was not investigated and the effect of added HClO_4 has already been studied [2,15].

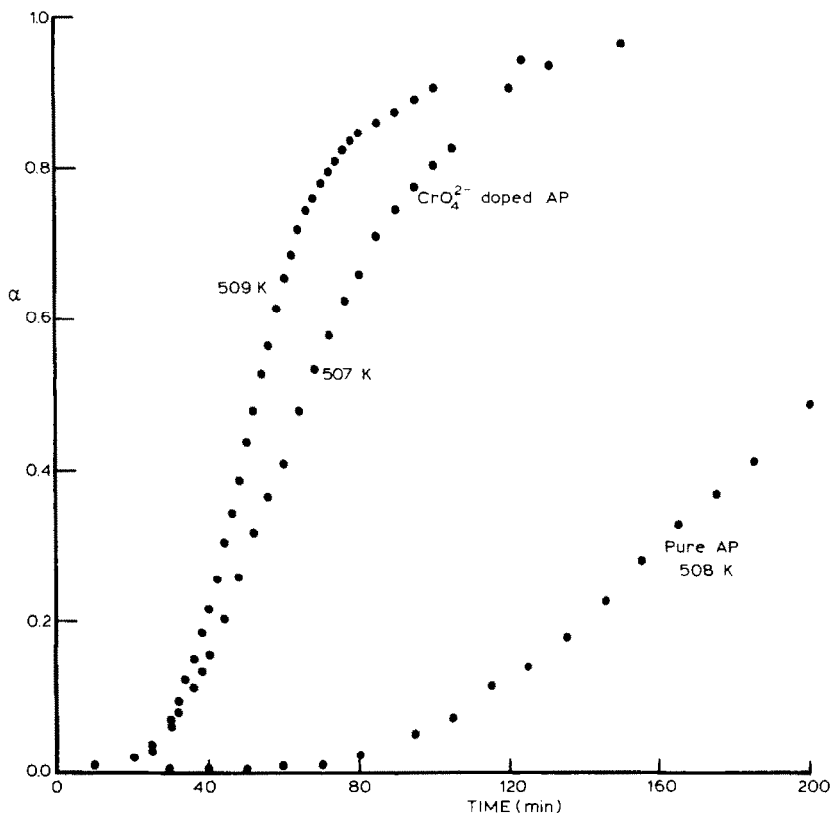


Fig. 2. Isothermal α -time curves for the thermal decompositions at 508 ± 1 K of single crystals of pure AP and CrO_4^{2-} -doped AP. The chromate ion reduces the induction period and accelerates the rate of subsequent decomposition.

It was observed that at higher temperatures (ca. 550 K, cubic AP [2,15]) with excess $\text{NH}_4\text{H}_2\text{PO}_4$ there was a relative increase in the amount of salt sublimed together with a diminution in the extent of decomposition. Again it is suggested that the effective dilution of the reacting entities reduces their ability to interact.

Chromate ion

It has been shown [16] that incorporation of CrO_4^{2-} into the crystal accelerates AP decomposition. The relatively perfect yellow AP crystals, of the usual habit, used to measure the decomposition kinetics here, were prepared by slow evaporation of an aqueous AP solution that contained 3% molar $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

We confirm (Fig. 2) the earlier observation [16] that incorporated CrO_4^{2-} markedly enhances the AP decomposition rate ($\times 3$ between $0.15 < \alpha < 0.7$). It also reduced the induction period to ca. 10 min at 508 K, or little more than the heating time for the reactant. Fractional reaction α vs. time curves

(for permanent gas evolution, a 78 K trap was present) were sigmoid shaped [4], evidence that the kinetic characteristics were not markedly changed by the additive. The extent of reaction (40% weight loss) was significantly greater than that for reaction of pure AP (28% weight loss). Microscopic examinations of the solid residue from completed decompositions revealed the presence of small opaque particles embedded in the reactant, identified as chromium oxide aggregations. The porous glass wool plug used to confine the reactant within its container was stained yellow, presumably due to volatilized CrO_2Cl_2 from the reaction.

We do not accept the previous conclusion [16] that chromate ions promote AP decomposition through an influence of light, because our reactions were conducted under conditions of very low illumination. We prefer an explanation consistent with our proposed mechanism [1], based on the known ability of chromate to oxidize ammonia [10]. CrO_4^{2-} incorporated in the lattice is perhaps first converted to the dichromate [20]. The reaction $2(\text{NH}_4)_2\text{CrO}_4 \rightarrow (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} + 2\text{NH}_3$ proceeds rapidly at reaction temperature. (There is no evidence that the NH_3 released increases [15] the induction period to AP decomposition.) Ammonium dichromate thus formed decomposes rapidly at 508 K and oxidizes NH_4^+ and/or NH_3 to NO_2^- and NO_3^- , the chromium thereby being reduced to lower oxide(s) that are retained in the residue. The oxidized nitrogen is regarded [1] as being capable of rapid conversion to NO_2ClO_4 . Thus the chromate additive is identified as being capable of producing the essential reaction intermediate. Consequently nucleation is rapid at a large number of sites and dense nucleation results in the rapid initial reaction and the ultimate decomposition of a relatively large proportion of the reactant. This comparison reveals interesting relationships between the decompositions of AP [1–4,15] and the ammonium chromates [10,20], the consistency gives confidence in the mechanistic conclusions reached for both reactions.

“Anhydrous AP”

Elemental analyses of the aqueous solution-grown AP crystals used in the previous study [1], showed these to contain a significant quantity of constituent water: $(\text{NH}_4^+)_{0.87}(\text{H}_3\text{O}^+)_{0.13}\text{ClO}_4^-$. It was of interest, therefore, to make a comparative decomposition study of the behaviour of a reactant having a composition closer to the stoichiometric ideal. The preparation referred to here as “anhydrous AP” was synthesized from (water free) dried NH_3 gas and anhydrous liquid HClO_4 . The flow of NH_3 gas was continued to give a white solid smelling of ammonia, which produced a strongly alkaline reaction in water. The composition of this preparation, measured identically to the solution-grown material [1], was $(\text{NH}_4^+)_{0.95}(\text{H}_3\text{O}^+)_{0.05}\text{ClO}_4^-$. It contained less water and was finely divided, composed of approximately spherical particles (diameters 50–100 μm , close to the particle size of maximum decomposition rate [15]).

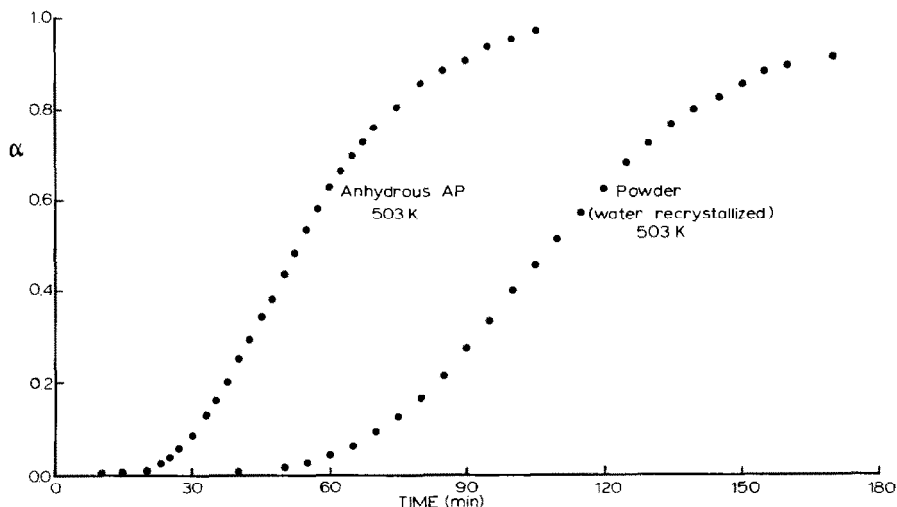


Fig. 3. α -time plots for the decomposition of anhydrous AP and of a water-recrystallized reactant of similar fine particle size at 503 K. Anhydrous AP decomposes at a significantly greater rate than the water-recrystallized reactant.

α -time plots for the decompositions of anhydrous AP and a crushed powder sample of similar particle size are compared in Fig. 3. The induction period is markedly shorter for the anhydrous AP. This is a most unexpected result because exposure of AP to ammonia has been shown [15] to increase the time required to initiate reaction. However, the observation here is consistent with the view [1] that the NO_2ClO_4 intermediate is highly susceptible to hydrolysis by available water and the constituent water is retained at or near the surface early in the reaction [12]. It follows, therefore, that in the anhydrous AP, nitryl perchlorate can be evolved relatively more rapidly to a concentration sufficient to initiate reaction. Similarly, the more rapid rate of subsequent decomposition of this preparation ($\times 2$, between $0.15 < \alpha < 0.7$) can be ascribed to reduced hydrolysis of the intermediate within the active fluid droplets that constitute the zone of chemical change. The water content of the residue from the completed decomposition of anhydrous AP was just detectably larger than this reactant. Thus a small proportion of the product water was retained in the residue and the concentration moved towards that characteristic of the solution-grown material.

CONCLUSIONS

The principal conclusion from the several investigations reported here is that the observations generally confirm, and are entirely consistent with, the conclusion that NO_2ClO_4 is the essential reaction intermediate in AP decomposition. Some of the results also appear to be in conflict with the

requirements of the proton transfer model. Our principal conclusions can be summarized as follows.

(1) Attempts to introduce NO_2ClO_4 on to the initial AP reactant surface were unsuccessful. This emphasizes the transitory existence of the intermediate under reaction conditions, it can only be effectively regenerated within the structure specifically developed and containing it during reaction propagation.

(2) The decomposition of the chromate ion incorporated in the AP lattice, capable of ammonia oxidation, markedly increased the reaction rate without changing the sigmoid-shaped α -time kinetic characteristics. This supports the view that the appearance of oxidized nitrogen is a nucleation step. The role of platinum metal is believed to be similar, this additive is also effective in promoting ammonia oxidation.

(3) The consequences of adding H_2SO_4 or H_3PO_4 on AP decomposition were always small. This is difficult to reconcile with the proton transfer mechanism, suggesting that the reported influence [15] of added HClO_4 is to be associated with its oxidized chlorine rather than its acidity.

(4) A reduction in the amount of constituent water incorporated in AP increased the decomposition rate. This is readily ascribed to a diminution in the extent of NO_2ClO_4 hydrolysis within the reaction zone. This observation (also the influence of ammonia [15], present in our reactant) is not explained by the proton transfer mechanism where anhydrous AP would have been expected to exhibit a prolonged induction period.

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