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Towards a more sustainable production of triacetoneamine with heterogeneous catalysis

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ABSTRACT

The acid-catalyzed condensation of acetone and ammonia to directly produce 2,2,6,6-tetramethy-4-piperidone (triacetonamine) was studied under both homogeneous and heterogeneous catalysis. The selectivity to the desired product was affected by the presence of a complex reaction network involving several kinetically parallel and consecutive reactions, leading to by-products such as diacetonealcohol, diacetoneamine, mesityl oxide, acetonine, and 2,2,4,6-tetramethyl-2,5-dihydropyridine. The latter was the most undesired by-product, since its formation was irreversible. Key elements in achieving high selectivity in the direct synthesis of triacetonamine were the molar feed ratio between acetone and ammonia, and the amount of water in the reaction medium; in fact, water was found to play an important role in the transformation of the intermediate acetonine into triacetonamine. Compared with homogeneous catalysis, the selectivity achieved by the use of the heterogeneous H-Y zeolites was controlled by means of a proper selection of the zeolite features. In fact, the use of a highly hydrophilic H-Y zeolite made it possible to achieve the same selectivity as that obtained under homogeneous catalysis conditions, with the additional advantage of using an easily separable and reusable catalyst, which showed no deactivation.

1. Introduction

2,2,6,6-Tetramethyl-4-piperidone (triacetonamine, TAA) is the key intermediate for the synthesis of polymer light stabilizers HALS (Hindered-Amines-Light-Stabilizers) [1,2]; their ability to efficiently interrupt polymer degradation by radical scavenging is based on the sterically hindered amine functional group, which is able to form stable N-oxides as active intermediates (Denisov cycle). TAA is also used in the synthesis of drugs, nitroxyl radicals of piperidine, and pyrrolidone derivatives [2]. For instance, by the oxidation of TAA or its derivatives, the corresponding tetramethylpiperidine-N-oxide, called TEMPO, is formed; the latter may be used as a polymerization inhibitor, molecular weight regulator, or oxidation catalyst.

In literature, various procedures are reported for the synthesis of TAA, with the most important being: (i) the direct condensation of acetone and ammonia (Scheme 1) [3–8], and (ii) the two-step process comprising the synthesis of 2,2,4,4,6-pentamethyl-1,2,5,6-tetrahydropyrimidine (acetonine, ACTN), carried out at room temperature, and the reaction of the separated ACTN with acetone or water to yield TAA [9,10]. Patent literature describes various catalysts for these reactions, such as homogeneous Lewis and Brønsted acids ($CaCl_2$, $ZnCl_2$, NH_4Cl, AlF_3, and BF_3, used especially in the second step of the two-step process) [10–13], sulfonated resins (Amberlyst® and Nafion®) [14] and *p*-nitrotoluene [15]. In the one-pot process, the catalysts used industrially are based on homogeneous systems (such as $CaCl_2$, NH_4NO_3 or NH_4Cl), because of their better performance, although the use of a heterogeneous system might offer two advantages: an easier separation of the catalyst from the reaction medium, and fewer problems related to product contamination. On the other hand, the heterogeneous catalyst should be easily regenerable and show constant performances during repeated uses or long time spans in the continuous-flow mode; in this respect, inorganic solid acids are preferable over organic resins.

Table 1 summarizes the yields to TAA reported in literature, using various catalysts and procedures. It is shown that the reaction of ACTN transformation into TAA – the second step in the two-step process – can be carried out with a remarkable yield, by using a Lewis or a Brønsted acid catalyst, depending on the reaction conditions used. The stoichiometry for the transformation of ACTN into TAA involves the elimination of either NH_3 replaced with H_2O, or

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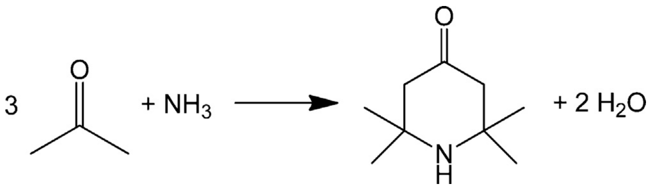
Table 1
Main catalysts and TAA yield in the two-step and one-pot process.

References	Starting materials	Catalyst	TAA yield (mol%)
[10]	ACTN, acetone	BF_3; NH_4Cl	95; 95 (wt.%)[a]
[11]	ACTN, acetone (+ water)	p-Toluenesulphonic acid salt of ACTN	91
[6]	ACTN, acetone	Acetyl halide	[b]
[13]	Acetone, NH_3	Acid ion exchanger, in continuous fixed-bed reactor	25[c]
[3]	Acetone (+ methanol), NH_3	CCl_4	26[c]
[4]	Acetone (+ methanol), NH_3	Organotin halides; cyanuric halides	36; 39[c]
[5]	Acetone, NH_3	$CaCl_2{\cdot}2H_2O$; NH_4Cl; $CaCl_2{\cdot}2H_2O + NH_4Cl$	20; 24; 28[c]
[14]	Acetone, NH_3	Perfluorinated sulphonic acids (Nafion®)	25[c]
[8]	Acetone, NH_3	Dimethyl sulfate	28[c]
[12,16]	Acetone, NH_3	$CaY + NH_4NO_3$	22[c]

[a] wt and mol yield, calculated with respect to initial ACTN, are very similar, because of the very similar MW of ACTN and TAA.
[b] Weight yields higher than 100% were claimed, probably referring to some unspecified TAA salt.
[c] Molar yield, calculated after the multiplication of the number of TAA moles by the factor 3.



Scheme 1. TAA synthesis stoichiometry in the one-pot process.

2-iminopropane (dimethylketimine) replaced with acetone. Therefore, the reaction can be carried out in any of three ways: in the presence of at least an equimolar amount of water, in the presence of excess acetone and without water (the preferred procedure), or with both acetone and water [6,10,11].

The case of the one-pot reaction is different, since several equilibria establish in the presence of acetone (or diacetonealcohol) and ammonia, and most reactions involved are equilibrium-limited. In fact, in most cases, the yield to TAA reported is in the range of 20–30%. Worthy of note is the outstanding TAA selectivity, higher than 95%, with a 22% yield: it was obtained by combining a very large amount of NH_4NO_3 (used both as a catalyst and as an ammonia source) with Ca-exchanged HY zeolite catalysts [12,16].

As shown in Scheme 1, water is not needed in the overall reaction stoichiometry, and in fact gaseous ammonia is typically used in industrial processes. On the other hand, a NH_4OH aqueous solution may also be used [16], clearly increasing the process safety, while the actual role of water on the reaction mechanism, as well as on yield and selectivity, has not yet been investigated in detail.

Despite the industrial importance of this compound, very little information is available in literature on the mechanism of TAA formation and the role of the main reaction parameters. We decided to investigate this reaction under both homogeneous and heterogeneous catalytic conditions; the final aim was that of designing a heterogeneous catalyst for the one-pot synthesis of TAA, using a NH_4OH aqueous solution as the ammonia source, and a properly selected and fully reusable solid acid catalyst, without the need for homogeneous co-catalysts.

2. Experimental

The following reactants and products were used for the reaction: Acetone (Chromasolv® Sigma–Aldrich), Ammonium Hydroxide 28–30 wt% (Sigma–Aldrich), Ammonium Chloride (99.5%+ Sigma–Aldrich). The zeolites were provided by TOSOH: HSZ-330HUA (HY zeolite SAR 6) 584 m^2/g (from catalogue 550 m^2/g), HSZ-390HUA (HY zeolite SAR 200) 814 m^2/g (from catalogue 750 m^2/g), and HSZ-360HUA (HY zeolite SAR 15, from catalogue 550 m^2/g). The H-β zeolite was supplied by Süd-Chemie (sample SN308 H/00, SAR 150). The ammonium-Y zeolite (SAR 15) was prepared by first exchanging the H-zeolite with Na^+ (treatment with a 2 M NaCl solution at 80 °C and pH adjusted at 10–11 with NaOH); then after filtration and drying at 110 °C, Na-zeolites were treated with 2 M NH_4Cl solution overnight and dried again at 110 °C.

For reactivity experiments, in a typical batch test, 2.3 g of acetone and a variable quantity of NH_4OH (30 wt%, aqueous solution) were loaded into a Teflon-capped test tube equipped with a magnetic stirrer. The mixture was homogenized at room temperature for 2–3 min and then the catalyst, either an ammonium salt (0.046 g) or a zeolite (0.23 g), was quickly added. The process was carried out at 65 °C while stirring at about 500 rpm. Diffusional limitations were excluded by means of preliminary experiments, carried out by varying the mixing speed.

Molar yields were calculated by dividing the concentration of a defined product by the initial molar concentration of acetone, normalized with respect to the number of C atoms. Molar selectivities were calculated by the ratio between the yield to a specific compound and acetone conversion.

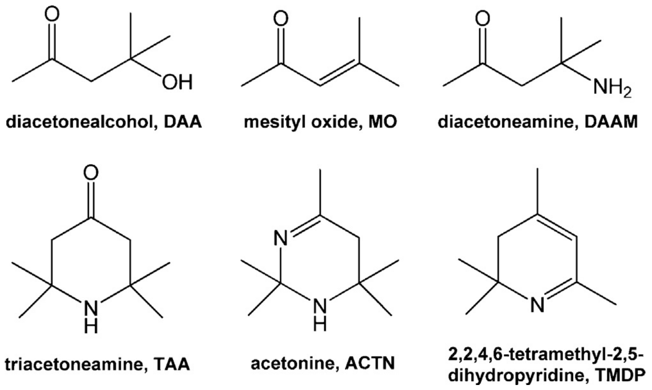
A continuous flow reactor with internal recirculation was also used for short-lifetime experiments; 3.0 g of zeolite in the form of extrudates (sample H-β 303 H/02, delivered by Süd-Chemie), were loaded, while a make-up feed consisting of acetone and NH_4OH aqueous solution in the desired molar ratio was introduced, and an analogous volumetric feed containing unconverted reactants and products was purged out from the reactor. The make-up/purge flows and the internally recirculated volumetric feed (withdrawn from the liquid buffer with an average composition equal to that of the purge stream) were set up in order to develop an overall reaction contact time of around 30 min.

At the end of the reaction, the mixture was analyzed by means of a Thermo Focus GC gas-chromatograph equipped with a FID detector and Agilent HP-5 column, using *n*-decane as the internal standard. Analysis conditions were: 50 °C for 2 min, 10 °C/min up to 280 °C, and 5 min at 280 °C.

3. Results and discussion

3.1. Determination of the reaction scheme in homogeneous catalysis

We first carried out a kinetic study at 65 °C, using an acetone-to-ammonia molar feed ratio equal to 4.0 and a catalyst-to-acetone weight ratio equal to 0.02, with a reaction time ranging from 0 to 120 h. Ammonium hydroxide (30 wt% aqueous solution) was used as a source of ammonia, and ammonium chloride as the catalyst. The reaction products, shown in Scheme 2, were: diacetonealcohol (DAA), diacetoneamine (DAAM), mesityl oxide (MO), acetonine (ACTN), triacetoneamine (TAA), and



Scheme 2. Reaction products of the acid-catalyzed condensation of acetone and ammonia.

2,2,4,6-tetramethyl-2,5-dihydropyridine (TMDP). The results of the reactivity experiments are shown in Fig. 1.

Since we fed an excess of acetone compared to the stoichiometric requirement, acetone conversion was not complete, but reached a stable value of 45–47%; indeed, the conversion of ammonia reached its maximum value already a few hours after the mixing of reactants and, correspondingly, acetone conversion also reached its maximum value. Thereafter, for longer reaction times, changes involved the distribution of products only. In this regard, the only kinetically primary products were DAAM and ACTN; in fact, the extrapolated selectivity to nil conversion was approximately 20% for DAAM and 55% for ACTN. However, the ACTN and DAAM selectivity rapidly declined while the conversion rose, with a concomitant increase in TAA selectivity. In short, after a rapid first step where the condensation of acetone and ammonia leads to ACTN and to DAAM, under the conditions used (T 65 °C), the two compounds convert into TAA. The transformation of ACTN into TAA may occur either with the insertion of water and elimination of ammonia, or, in the presence of acetone, with acetone insertion and elimination of 2-iminopropane. Scheme 3 shows an hypothetical mechanism for interconversion between the two compounds.

Moreover, TAA selectivity dropped at long reaction times, whereas TMDP selectivity continued to increase throughout the entire experiment. After 120 h reaction time, TMDP was the prevailing product; therefore, it is possible to assume that reactions leading to TMDP formation are irreversible. In other words, after a proper reaction time, TMDP would be the unique product of the process. In regard to the formation of TMDP, the selectivity trend shown in Fig. 1 suggests that it forms by consecutive transformation of TAA via water elimination, even though a direct transformation of ACTN via ammonia elimination cannot be excluded. Indeed, the dehydration of TAA may proceed through a series of steps which involves (a) ring opening of TAA to a enol/imine form; (b) tautomerization to the keto/enamine form; (c) ring closure to a cyclic "aldiminol" (the equivalent of a cyclic aldol); and (d) dehydration, which under basic conditions may proceed via an E1cB mechanism (Scheme 4). The last step, as is known in aldol condensations, may well be irreversible, thus explaining the continuous increase of TMDP selectivity.

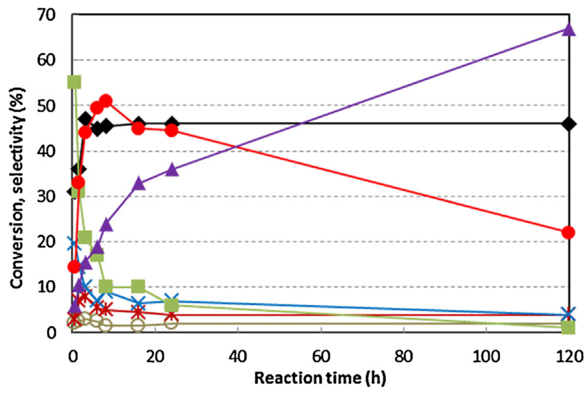


Fig. 1. Acetone conversion and selectivity to products in the presence of NH_4Cl catalyst in function of reaction time. Reaction conditions: acetone/ammonia mol. ratio 4.0, catalyst/acetone wt ratio 0.02, T 65 °C. Symbols: (♦) Acetone conversion (%). Selectivity (%) to: (●) TAA, (■) ACTN, (▲) TMDP, (○) DAA, (✱) MO, and (×) DAAM.

The overall reaction scheme, as inferred from kinetic experiments, is shown in Scheme 5. It is worth noting that the reaction network consists of several reversible reactions, with the exception of formation of TMDP. This means that all reaction intermediates may potentially be converted into the desired TAA while, on the other hand, TMDP is a waste compound, since it cannot be transformed back into TAA. In other words, the key feature of the process is not the selectivity to the desired product (TAA), but the selectivity to the undesired TMDP, which should be as low as possible. Therefore, the key element for an efficient synthesis of TAA is the kinetic control over the consecutive and irreversible reaction of TMDP formation.

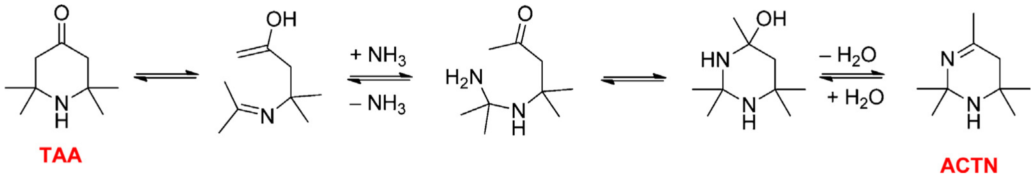
3.2. *Effect of the acetone–ammonia molar feed ratio*

The effect of the amount of ammonia in the reaction medium was also investigated. The reaction kinetics was studied at 65 °C, with a catalyst-to-acetone weight ratio equal to 0.02. Two more acetone-to-ammonia molar feed ratios (2.5 and 10.0) were tested. As shown in the plots of Fig. 2, the final acetone conversion was greatly affected by the amount of ammonia fed in the process. In the case of the acetone–ammonia molar ratio 2.5 (Fig. 2, top), the conversion reached 60% in a few hours, with high selectivity to the primary product ACTN (70%). On the other hand, ACTN was converted with low selectivity into TAA, at the same time fostering TMDP formation. Opposite results were achieved with a high acetone-to-ammonia molar feed ratio (10.0) (Fig. 2, bottom). In this case, because of the large excess of acetone used, the conversion of acetone was quite low (about 30%), with good selectivity to the primary product ACTN (40%), but the subsequent transformation of the latter was much more selective to TAA, if compared to the reaction at high ammonia concentration (lower acetone-to-ammonia molar ratio).

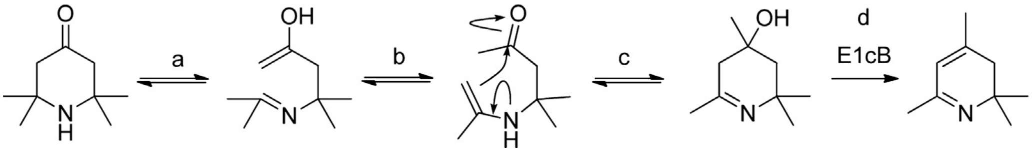
Fig. 3 summarizes the above considerations, while comparing the product selectivity resulting from different molar feed ratios at similar conversions (results taken from Figs. 1 and 2); selectivity to TAA achieved when the maximum conversion of acetone was reached is also reported. This figure clearly shows an important conclusion: the reactant feed ratio greatly affected process selectivity and is an important parameter for TAA production. In fact, it seems more convenient to carry out the process at low conversion (that is, at a high acetone–ammonia molar ratio) by recycling the reaction mixture after the separation of TAA, than to use low feed ratios (e.g. close to the stoichiometric ratio 3), with the aim of fostering acetone conversion. The former conditions would ensure greater amounts of TAA in the outgoing stream with lower separation costs.

3.3. *The role of water in homogeneous catalysis*

According to our results, the key point for the control of TAA selectivity is limit the rate of formation of the undesired TMDP compared to the rate of TAA formation (Scheme 5). From the reaction stoichiometries, one can infer that water may play an important role in the control of selectivity, since it is involved in the key



Scheme 3. An hypothetical mechanism for interconversion of TAA and ACTN.



Scheme 4. An hypothesis about the mechanism for the irreversible transformation of TAA into TMDP.

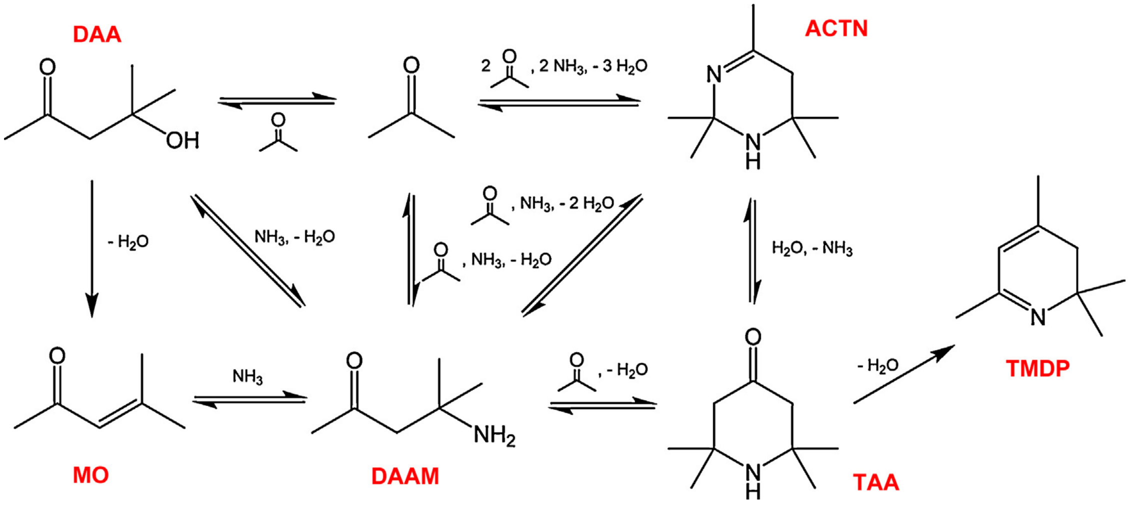
reaction of ACTN transformation into TAA; indeed, this is the only reaction, amongst all direct reactions shown in Scheme 5, where water is a reactant, in all other cases being a co-product. Even in the case of DAAM transformation into TAA, water is eliminated during the condensation reaction; however, this reaction contributes less to TAA formation than that starting from ACTN, due to the lower initial DAAM selectivity. According to patent literature, the ACTN transformation into TAA may be carried out either without water in the presence of acetone, or without acetone in the presence of water [6,10,11]. On the other hand, the role of water in the one-pot process has not yet been clearly demonstrated. Fig. 4 shows a comparison between the reaction carried out under the usual conditions (acetone-to-ammonia molar feed ratio 4.0, *T* 65 °C) and the same reaction conducted in the presence of anhydrous sodium sulphate as the dehydrating agent; it is worth noting that the amount of salt added was calculated so as to completely remove water from the reaction medium.

Fig. 4 demonstrates that the biggest difference between the two experiments concerned the yields to ACTN and TAA. In fact, water removal decreased the rate of ACTN transformation to TAA (the sum of yields to the compounds remained the same): a clear indication that the formation of TAA was accelerated in the presence of water. On the other hand, the yield of TMDP was not affected so much; in fact, its formation does not involve a contribution from water. In conclusion, water is essential for promoting the formation of TAA, and for obtaining a higher TAA/TMDP selectivity ratio. We also carried out an experiment adding twice as much water than that already present when the NH_4OH/H_2O solution was used; however, we did not observe any significant effect, thus indicating that the amount of water available from ammonia solution is sufficient to observe the selectivity enhancement effect.

3.4. The role of ammonium: acid catalysis in alkaline (NH_4OH/H_2O) reaction medium

The ammonia source used for catalytic experiments was NH_4OH in aqueous solution (the K_b value for NH_3 hydration with water dissociation is as low as 1.85×10^{-5}). In order to better understand the role of the ammonium ion in the salt used as the homogeneous catalyst, specific tests were carried out under the following conditions: acetone-to-ammonia molar ratio 4.0, temperature 65 °C, catalyst-to-acetone ratio wt. 0.02, while using various catalysts.

As shown in Table 2, the blank test (reaction with only acetone and NH_4OH) gave little conversion of acetone with traces of DAA only (aldol condensation in alkaline conditions), and small amounts of ACTN. On the other hand, however, no reaction occurred when only acetone and NH_4NO_3/H_2O were used (the latter with the same molar amount as for the ammonium hydroxide used previously). This means that the co-presence of both NH_3 and NH_4^+ is needed to carry out this reaction. It is important to note that the K_a value for ammonium ion in water is equal to 5.6×10^{-10}; therefore NH_4^+ is a weak Brønsted acid. When the reaction was carried out under basic conditions, achieved by means of NaOH 50 wt%, there was a low acetone conversion, with a formation of DAA and traces of



Scheme 5. Reaction scheme of TAA synthesis by direct reaction between acetone and ammonia.

Table 2
Acetone conversion (%) and yield to products (%) in function of base source and catalyst.

Base, catalyst	Conv.	TAA yield	ACTN yield	TMDP yield	Others yield
NH_4OH, no	5	0	4	0	1
NH_4OH, NH_4Cl	45	22.5	7.5	8.5	6
NH_4NO_3, no	0	0	0	0	0
NH_4OH, NH_4NO_3	42	21	5	8	8
NaOH, no[a]	5	0	0	0	5
NaOH, NH_4NO_3	12	0	0	0	12

Reaction conditions: temperature 65 °C, catalyst/acetone wt ratio 0.02, reaction time 6 h, acetone/ammonia mol. ratio 4.0. Others: MO + DAA + DAAM.

[a] NaOH 50 wt% replacing ammonium hydroxide.

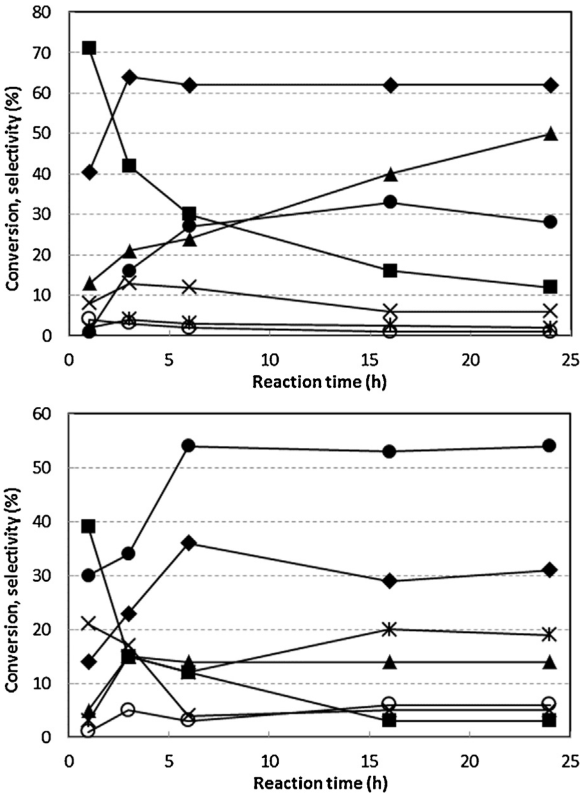


Fig. 2. Acetone conversion and selectivity to products in the presence of NH_4Cl catalyst and with different acetone/ammonia molar ratios in function of reaction time. Top: acetone/ammonia mol. ratio 2.5. Bottom: acetone/ammonia mol. ratio 10.0. Reaction conditions: T 65 °C, catalyst/acetone wt ratio 0.02. Symbols: (◆) Acetone conversion (%). Selectivity (%) to: (●) TAA, (■) ACTN, (▲) TMDP, (○) DAA, (✳) MO, and (×) DAAM.

MO only. After the addition of a catalytic amount of an ammonium salt, the conversion of acetone increased (from 5% to 12%), with higher DAA and MO yields. Thus the ammonium ion shows the catalytic activity for the aldol condensation of acetone also, even in the presence of a strong base. In conclusion, it is important to note that the ammonium ion is the only acid specie that exists in an ammonia environment. In other words, whichever Brønsted acid is used as the reaction catalyst, it immediately reacts with ammonia, thus generating in situ the corresponding ammonium cation (a weaker acid species). Table 2 also shows that using either NH_4Cl or NH_4NO_3 led to quite similar results, evidencing a negligible anion effect for ammonium salts of strong acids.

Since the main primary product of the reaction was ACTN, it is reasonable to assume the presence of a mechanism involving a very reactive intermediate species, e.g. 2-iminopropane (dimethylketimine). The latter may be formed by the direct condensation of acetone and ammonia. In this case, the ammonium ion acts by coordinating the carbonylic moiety and making it more prone to the attack of ammonia. Moreover, the co-presence of stable acid sites (ammonium ion) and ammonia makes possible the occurrence of several reactions at the very beginning of the process. Indeed, the formation of various aldol condensation compounds

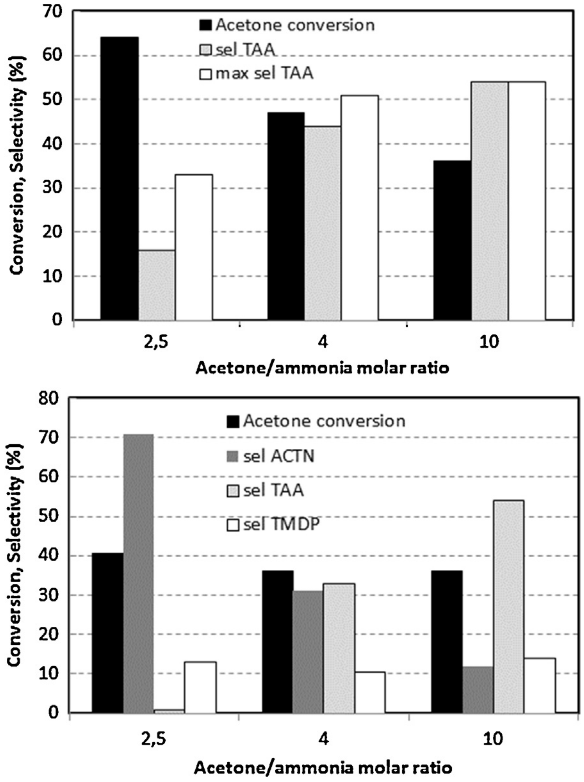


Fig. 3. Comparison of catalytic behaviour for different acetone/ammonia molar ratios at the maximum acetone and ammonia conversion (top), and for similar acetone conversions (bottom), in the presence of NH_4Cl catalyst. Other conditions as in Figs. 1 and 2.

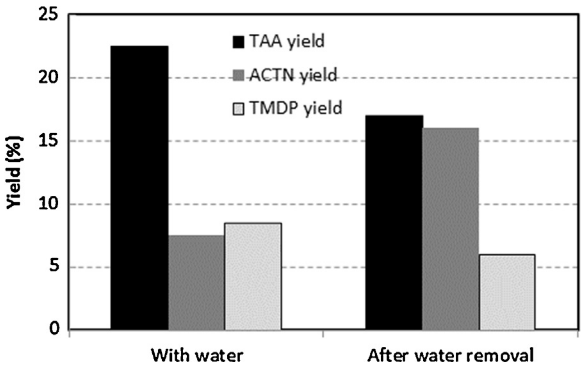
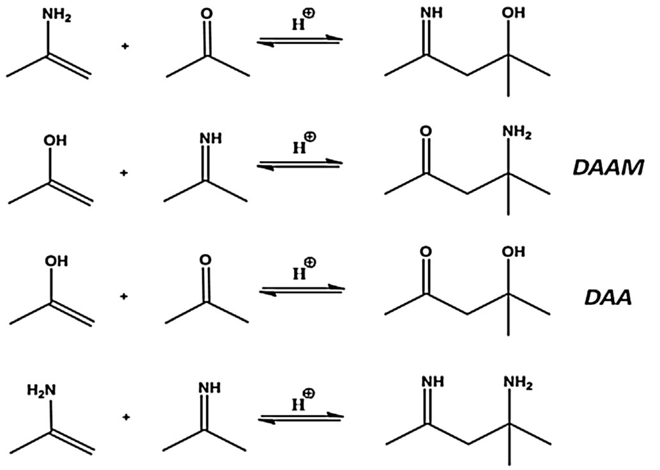
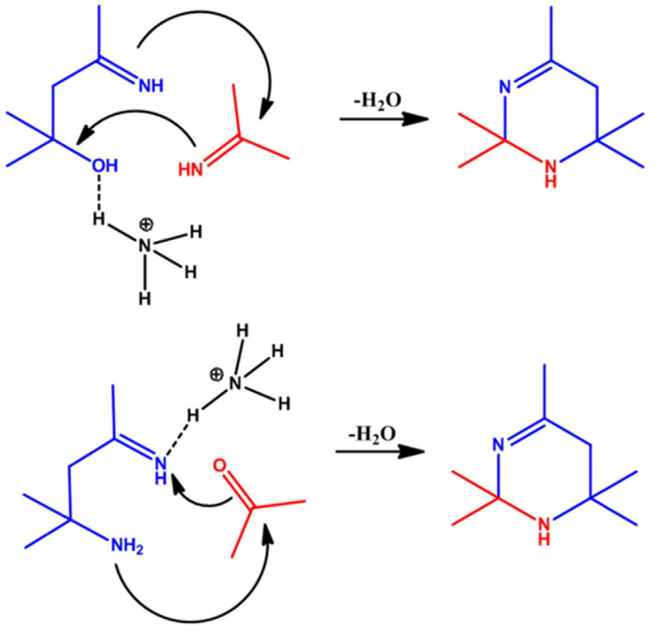


Fig. 4. Effect of water removal by anhydrous sodium sulfate in the presence of NH_4Cl catalyst. Reaction conditions: T 65 °C, acetone/ammonia mol. ratio 4.0, catalyst/acetone wt ratio 0.02, and reaction time 6 h.



Scheme 6. Aldol condensation of acetone and dimethylketimine (or the corresponding enolic forms).

by reaction with the corresponding enolic or enaminic forms is possible, as summarized in Scheme 6. DAAM and DAA were the most stable aldol condensation compounds, a fact that made it possible to obtain them as reaction products, whereas the very reactive imino species immediately underwent consecutive transformations by reaction with either acetone or 2-iminopropane, and were not isolated as intermediate compounds. The driving force of the consecutive reaction was the formation of the cyclic ACTN. In this case, too, the role of the ammonium ion is probably crucial in catalyzing ACTN formation, as proposed in the hypothetical mechanism shown in Scheme 7. A catalytic test carried out by using DAA as reagent, in the presence of ammonium hydroxide and ammonium salt catalysts, confirmed this hypothesis because the main product obtained was acetone (40% yield), with lower amounts of other compounds (DAAM, ACTN, TAA, and others). This means that the starting point for obtaining N-containing compounds is acetone, and not DAA, although the latter may be used as a reactant, because it may reversibly yield acetone.



Scheme 7. Hypothetical intermediates and mechanism in ACTN formation.

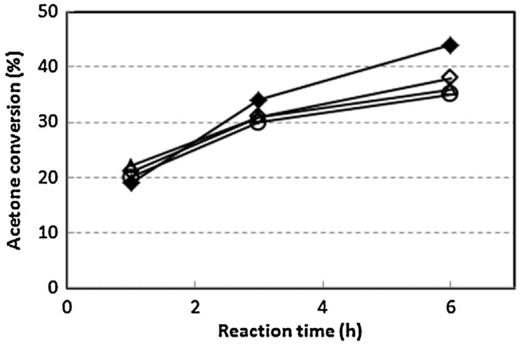


Fig. 5. Acetone conversion in function of reaction time. Symbols: catalyst HY-6 (△), HY-15 (◊), HY-200 (○), and NH_4Y-15 (♦). Reaction conditions: acetone/ammonia mol. ratio 4.0, catalyst/acetone wt ratio 0.10, T 65 °C.

3.5. Heterogeneous catalysis with zeolites

One of the drawbacks of the homogeneous catalysis is the difficulty of catalyst recovery; complete catalyst recovery is extremely important if the catalyst is expensive and/or toxic. In TAA synthesis, ammonium salts such as NH_4Cl are not expensive, but must be separated and processed after reaction, with the aim of avoiding product contamination. Therefore, an easily separated, heterogeneous catalyst would be an important achievement.

As shown in Table 1, heterogeneous catalysts have also been claimed for the one-pot synthesis of TAA, based mainly on organic sulfonated resins. The only report on the use of an inorganic solid acid deals with an attempt of combining the Lewis acid properties of Ca^{2+} cation in a Y zeolite, and the efficient homogeneous properties of the ammonium cation [12,16]. In the latter case, the use of a very large amount of ammonium salt made it possible to operate under mild temperature conditions (those typically used for the synthesis of ACTN, the first step in the two-step process), thus achieving a remarkably high selectivity to TAA, but still with the low TAA yield typically obtained in this reaction.

Having established the crucial role of the ammonium cation in the reaction, we decided to use commercial zeolites, both in the acid form and after the exchange of protons with ammonium cations (see details in Section 2 regarding the procedure for the preparation of the exchanged Y zeolite). In fact, we hypothesized that, in the presence of NH_3/H_2O, the rapid generation of the ammonium cation might promote the in situ development of active sites with the desired acid strength.

Fig. 5 compares the conversion based on reaction time, achieved for H-Y zeolites having different silica-to-alumina ratios (SAR). It is possible to notice that the activity of the H-Y zeolites was not much affected by the SAR; moreover, the Y zeolite with SAR equal to 15 showed a similar activity when used either in the proton or in the ammonium form. All these data suggest that the rate-limiting step of the process might be either the intraparticle diffusion of reactants or the counterdiffusion of products, due to the very high reaction rate compared to the diffusion rate. On the other hand, it must be remembered that the acidity of the H-Y zeolites in basic (NH_3) aqueous medium is levelled off due to the presence of ammonia and water. Nevertheless, the quick generation of the ammonium cation in acidic zeolites ensured a rapid reaction kinetics, similar to that shown with the pre-prepared ammonium form of the same zeolite.

On the other hand, the distribution of products was affected by catalyst features, as shown in Table 3, which compares the selectivity to the main products (ACTN, TAA and TMDP), for similar values of acetone conversion. Fig. 6 details the effect of reaction time on the selectivity to the various products, for HY-6 and HY-200 samples. In this case also, as for the NH_4Cl catalyst, the primary product ACTN

Table 3
Acetone conversion (%) and selectivity to products (%) for experiments conducted with zeolites.

Catalyst	Reaction time (h)	Conv.	TAA	ACTN	TMDP
HY-6	6, 17	36, 40	15, 27	42, 26	5, 14
HY-15	6, 17	38, 43	14, 22	42, 24	13, 25
HY-200	6, 17	35, 42	12, 19	42, 25	12, 28
Hβ-150	6	56	4	56	5
NH_4Y-15	6	44	10	72	6

Reaction conditions: temperature 65 °C, catalyst/acetone wt ratio 0.10, reaction time 6 h, acetone/ammonia mol. ratio 4.0 (except Hβ, mol ratio 2.5).

was converted into TAA. The selectivity to TAA and TMDP was considerably affected by the SAR: in particular, the formation of TMDP was fostered by the HY-200 catalyst. As also shown in Table 3, an increase in the SAR led to a decreased selectivity to TAA and a corresponding higher selectivity to TMDP. The effect shown may be interpreted considering that the higher the SAR in the H-Y zeolite is, the lower its hydrophilicity, and vice versa [17–21]. Therefore, the behaviour shown is in accordance with the homogeneous catalysis data: in the more hydrophobic HY-200 zeolite, the water molecules necessary to convert ACTN into TAA are less available within the zeolite pores, while the competitive reaction of TMDP formation is kinetically more facilitated than that of TAA formation.

With regard to the performance of the ammonium-Y, a difference can be seen from the comparison between HY-15 and NH_4Y-15 (Table 3); despite their similar activity (Fig. 5), the consecutive transformation of the intermediately formed ACTN into TAA and then TMDP was hindered, compared to the H-Y zeolite.

These data indicate that the generation of the $Z^- \ NH_4^+$ ion pair, the formation of the protonated dimethylketimine (occurring by incorporation of the ammonium cation from the zeolite, a reaction whose rate may be a function of the acid strength) [22,23] and the further reaction of the adsorbed imine into the key intermediate compound, ACTN, are all only marginally affected by the acidity features. Conversely, the further transformation of ACTN (which diffuses into the liquid phase and then undergoes consecutive reactions) may be affected both by zeolite features and by the nature of the active site.

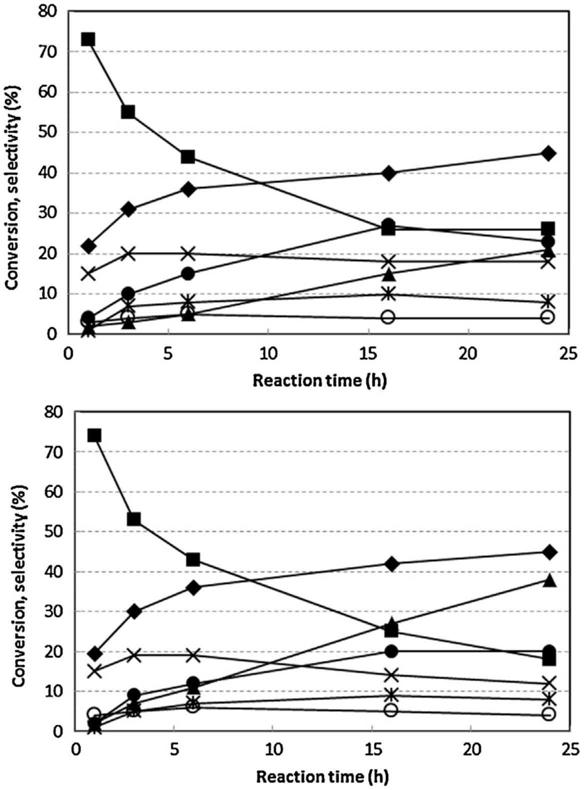


Fig. 6. Acetone conversion and selectivity to products in the presence of HY-6 (top) and HY-200 (bottom) zeolites in function of reaction time. Reaction conditions: acetone/ammonia mol. ratio 4.0, catalyst/acetone wt ratio 0.10, T 65 °C. Symbols: (◆) Acetone conversion (%). Selectivity (%) to: (●) TAA, (■) ACTN, (▲) TMDP, (○) DAA, (✱) MO, and (×) DAAM.

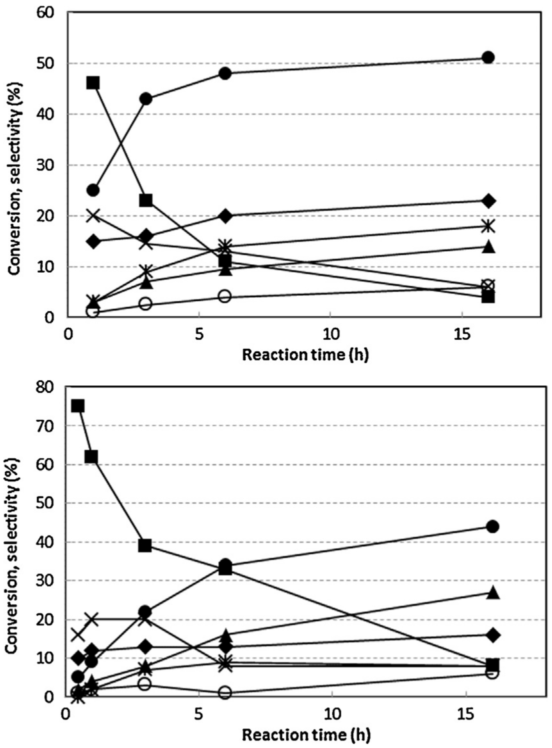


Fig. 7. Acetone conversion and selectivity to products as functions of time with HY-6 (Top) and HY-200 (Bottom) zeolites. Reaction conditions: acetone/ammonia mol. ratio 10.0, catalyst/acetone wt ratio 0.10, T 65 °C. Symbols: (◆) Acetone conversion (%). Selectivity (%) to: (●) TAA, (■) ACTN, (▲) TMDP, (○) DAA, (✱) MO, and (×) DAAM.

Table 4
Acetone conversion (%) and selectivity to main products (%) with the HY-6 zeolite.

T (°C), t (h)	Conv.	TAA	ACTN	TMDP
65, 6	20	48	11	10
45, 24	19	40	14	14
25, 72	17	14	49	8
25, 24[a]	17	29	36	6

Reaction conditions: catalyst/acetone wt ratio 0.10, acetone/ammonia mol. ratio 10.0.

[a] Catalyst 50 wt%.

Shown in Table 3 are also the results obtained with a Hβ zeolite. The peculiarity of this zeolite was its high selectivity to ACTN, and a low selectivity to consecutive by-products, despite the high acetone conversion. Thus, this zeolite type would be more suited to use for the first step of the two-step process, where the first step is aimed at the production of ACTN.

We finally used the more advantageous acetone–ammonia molar feed ratio (equal to 10.0); results for HY-6 and HY-200 are shown in Fig. 7. This shows that not only was the rate of ACTN transformation into consecutive products greatly accelerated with HY-6 (Fig. 7, top) as compared to HY-200 (Fig. 7, bottom), but the selectivity ratio between TAA and TMDP was also notably greater.

The effect of the reaction temperature on the catalytic behaviour of the HY-6 zeolite is shown in Table 4; experiments were conducted under conditions aimed at achieving comparable values of acetone conversion, i.e. using longer reaction times when lower temperatures were used. The most remarkable effect was a higher selectivity to ACTN, and a correspondingly lower selectivity to TAA (that to TMDP being less affected), when the reaction temperature was decreased. This agrees with literature claims that in order to limit consecutive transformations occurring on ACTN, and lastly to obtain high selectivity to this compound (the first step in the two-step process), it is necessary to use low reaction temperatures, at least with homogeneous catalysts.

Figs. 2 (bottom) and 7 (top) make it possible to compare the catalytic behaviour shown by NH_4Cl and by the HY-6 zeolite, which was the one showing the best performance among the heterogeneous systems investigated. When homogeneous catalysis is used, the TAA-to-TMDP selectivity ratio can be tuned by optimizing the acetone-to-ammonia molar feed ratio, whereas in heterogeneous catalysis with zeolites the effect of this parameter is not straightforward, since the effective concentration within the zeolite pores is greatly affected by zeolite characteristics. However, our results demonstrate that by combining the best acetone-to-ammonia molar feed ratio of 10.0, as inferred from homogeneous catalysis experiments, with the best zeolite (HY-6), it is possible to obtain a catalytic performance which is very similar to that observed with the homogeneous system (Fig. 2, bottom). Indeed, it is shown that when a low acetone/ammonia ratio was used, the catalytic behaviour was clearly better with homogeneous catalysis than with HY zeolites. However, when the high feed ratio – i.e. the one leading to the best selectivity to TAA under homogeneous catalysis conditions – was used, the catalytic behaviour was still worse with the HY-200 zeolite than with the homogeneous system, but became similar to the latter one when the HY-6 zeolite was used.

With regard to the reusability of the zeolite catalyst, we noted that when the formation of TMDP was low, after reaction the catalyst appeared slightly yellowish, and could be reused without any post-treatment, showing no variation in catalytic behaviour. Conversely, when the amount of TMDP formed was non-negligible, the catalyst turned red, because of the surface adsorption of TMDP, and in this case a washing treatment with acetone was needed before reusing the catalyst; for instance, with the HY-6 zeolite showing 9.6 ± 0.3 TAA% yield in the first use (Table 4), the same catalyst gave $9.3 \pm 0.3\%$ in the second and $9.8 \pm 0.3\%$ in the third use.

Additional experiments conducted in a fixed-bed, continuous-flow reactor, with recirculation of the liquid phase and continuous make-up of the fresh solution containing both acetone and ammonium hydroxide aqueous solution, offered a better assessment of the absence of any catalyst deactivation. In this case, the reaction was carried out at 45–50 °C, to minimize evaporation phenomena causing gas accumulation problems in the reactor head, while keeping the recirculation rate – referring to the purge/make-up flow rate – very high in order to permit a 35% acetone conversion. The catalyst was the Hβ, in the form of extrudates; we chose this catalyst because of its peculiar behaviour (Table 3), with high selectivity to ACTN. The reaction was carried out for 10 h. At the beginning, during the first few hours of reaction, the concentration of the various products increased in the recirculated liquid, because it was necessary to reach a steady-state concentration of all components in the reactor hold-up. After approximately 2 h, the steady-state behaviour of the reactor was reached, and the composition of the recirculated liquid remained constant (because the amount of the product withdrawn within the purge stream equalled the amount generated by the reaction), providing no catalyst deactivation phenomenon occurred. In fact, under the conditions used, the prevailing product was ACTN, and we registered a constant $34.0 \pm 0.2\%$ ACTN yield, $2.2 \pm 0.1\%$ DAA yield, 0.4% TAA yield, 0.15% MO yield, and 0.1% TMDP yield over a reaction time of 10 h. The formation of TMDP was low, but a strong interaction of TMDP with the zeolite would have caused a catalyst deactivation over time. Conversely, the zeolite maintained its activity over time, and there was no change in colour. It is also possible that the continuous flow of the reaction mixture over the fixed-bed allowed a rapid desorption of products (an event which, conversely, is more hindered when the reaction is carried out in the batch reactor), thus keeping the catalyst surface clean.

4. Conclusions

In this work, the direct synthesis of 2,2,6,6-tetramethy-4-oxopiperidone (triacetonamine, TAA) from acetone and ammonium hydroxide aqueous solution was investigated in the liquid phase. The reaction network includes parallel and consecutive reactions, most of which are reversible. This means that the key element is the minimization of the consecutive (and irreversible) reaction leading to the undesired 2,2,4,6-tetramethyl-2,5-dihydropyridine (TMDP) formation.

The acetone/ammonia ratio notably affected the process performance; the best results in terms of selectivity to TAA were obtained by using the higher acetone/ammonia ratio, with the homogeneous NH_4Cl catalyst. Water played an important role in the selectivity, especially in the ratio between TAA and TMDP.

HY zeolites with different features (SAR ratio and thus different hydrophilicity characteristics) led to different behaviours. The best selectivity was obtained by combining the more hydrophilic zeolite HY-6 (with lower SAR ratio) with the higher acetone–ammonia molar feed ratio. This behaviour was quite similar to that obtained with the homogeneous catalyst, but presented the further advantage of an easily separable and reusable catalyst.

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