Vapor-phase Beckmann rearrangement of cyclohexanone oxime over halide cluster catalysts

Sayoko Nagashima[a], Satoshi Kamiguchi[b,*], Satoshi Ohguchi[a,b], Teiji Chihara[a]

[a] Graduate School of Science and Engineering, Saitama University, Shimo-Okubo, Sakura-ku, Saitama City, Saitama 338-8570, Japan
[b] RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

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ABSTRACT

When a silica gel-supported tungsten halide cluster with an octahedral metal framework, $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O/SiO_2$, is treated in a helium stream in the temperature range 250–350 °C, catalytic activity for the Beckmann rearrangement of cyclohexanone oxime develops. Niobium and tantalum clusters with the same metal framework also catalyze the reaction. Cyclopentanone oxime and acetone oxime also undergo Beckmann rearrangements over the tungsten cluster. The weak Brønsted acidity ($H_0 \approx +1.5$) of the hydroxo ligand, which is developed on the activated cluster, is favorable for the rearrangement.
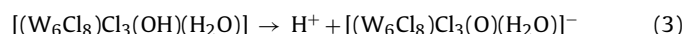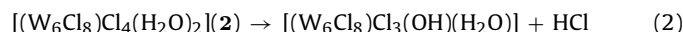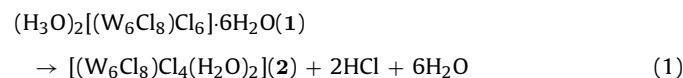
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1. Introduction

The Beckmann rearrangement is used for the industrial synthesis of azepan-2-one (ε-caprolactam), which is the starting material for nylon 6. The rearrangement is performed in the liquid phase using an excess amount of fuming sulfuric acid as a promoter, followed by neutralization of the acid with ammonia [1]. This process has serious disadvantages such as corrosion of equipment by the strong acid and by-production of a large amount of ammonium sulfate. To circumvent these issues, alternative catalytic vapor-phase Beckmann rearrangements have been developed using solid acids such as silica–alumina [2], boria [3], and Ta_2O_5/SiO_2 [4]. Various zeolites such as HNaY [5], H-USY [6], H-beta [7], H-MCM-41, H-FSM-16 [8], and MFI [9,10] have also been applied to the reaction, and the weak acidity of these catalysts is reported to be favorable for the reaction.

We have been studying the utilization of halide clusters as catalysts, although the application of the clusters to catalysis has not been reported since the first report on the synthesis of molybdenum(II) chloride in 1859 [11]. The halide clusters have characteristic features such as multi-center and multi-electron systems, unique intermediate oxidation states of the metal atoms, high thermal stability, high melting point, high boiling point, and low

vapor pressure as molecular metal halides. Taking these features into consideration, we have applied a wide variety of reactions to the halide clusters [12–17]. One of the specific aspects of halide cluster catalysis is Brønsted acidity [18,19]. In the case of the tungsten chloride cluster, $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ (1), formation of the Brønsted acid sites is interpreted as follows: when 1 is thermally treated in a helium stream, it changes to an aqua cluster $[(W_6Cl_8)Cl_4(H_2O)_2]$ (2) at 150 °C (Eq. (1)) and successively to a hydroxo cluster $[(W_6Cl_8)Cl_3(OH)(H_2O)]$ above 250 °C by releasing hydrogen chloride, without decomposition of the cluster framework (Eq. (2)) [12,20]. The hydroxo cluster exhibits Brønsted acidity (Eq. (3)), which has been confirmed by IR analysis of adsorbed pyridine [18]. Thus, we applied the halide clusters to the vapor-phase Beckmann rearrangement, and the results are shown in this report. The acid strength of the clusters is also reported.

$$(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O(\mathbf{1})$$
$$\rightarrow [(W_6Cl_8)Cl_4(H_2O)_2](\mathbf{2}) + 2HCl + 6H_2O \quad (1)$$

$$[(W_6Cl_8)Cl_4(H_2O)_2](\mathbf{2}) \rightarrow [(W_6Cl_8)Cl_3(OH)(H_2O)] + HCl \quad (2)$$

$$[(W_6Cl_8)Cl_3(OH)(H_2O)] \rightarrow H^+ + [(W_6Cl_8)Cl_3(O)(H_2O)]^- \quad (3)$$

2. Experimental

Crystals of molecular cluster complexes $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ [21], $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot6H_2O$ [22], $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot$

* Corresponding author. Tel.: +81 48 467 9401; fax: +81 48 462 4631.
E-mail address: kamigu@riken.jp (S. Kamiguchi).

$4H_2O$ [21], and $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ (**1**) [23] were synthesized according to the published procedures. The cluster Re_3Cl_9 was a commercial product (Furuya Metal Co. Ltd, Japan), and was used without further purification.

The general procedure for the preparation of the silica-supported catalyst is described in detail for **1**. Methanol (330 mL) was added to a 1 L flask containing **1** (1.0 g). After dissolution of the cluster, silica gel (Nippon Aerosil, Tokyo, Aerosil 380 m^2/g, 19.0 g) was added and allowed to stand for 1 h with occasional shaking. Then the solvent was evaporated to dryness under vacuum at ambient temperature. Samples of the dried silica gel were crushed and screened to 150–200 mesh. All of the clusters were supported on the silica gel in the same way at 5.0% by weight. All of the organic compounds were commercially available and used as received.

The general procedure for the catalytic reaction is described in detail for the system **1**/cyclohexanone oxime/methanol. A conventional vertical glass fixed-bed microreactor with a continuous gas flow system was operated at atmospheric pressure [12]. In each experiment, a weighed fresh catalyst sample of **1** (10 mg) was packed in a borosilicate glass tube (6 mm i.d.) with the aid of quartz glass wool and placed in the center of an electric furnace. The catalyst was initially heated from room temperature to a fixed temperature between 100 and 450 °C in 15 min in a helium stream (1.2 L/h), and then it was held at this temperature for 45 min. The reaction was initiated by feeding a methanol solution of cyclohexanone oxime (17 mol%, 200 μL/h, 0.65 mmol/h) into the helium stream using a syringe pump without changing the temperature. The reaction was monitored every 30 min by sampling the reaction gas (1 mL) with a six-way valve maintained at 200 °C, followed by analysis using an on-line GLC (methylsilicone G-column). The reactor effluent was frozen in a dry-ice trap for subsequent analyses with GLC (dimethylpolysiloxane capillary column) and GC/MS (dimethylpolysiloxane capillary column). Catalytic reactions using the other catalysts were performed in the same way. In this article, conversion and selectivity are defined as follows: conversion = products/(products + recovered cyclohexanone oxime) × 100 (%), and selectivity = product/(total amount of products) × 100 (%).

Acid strength of **1**/SiO$_2$ treated at 150 and 300 °C was determined by titration with butylamine [24,25]. The Hammett indicators used were 4′-dimethylaminoazobenzene-2-carboxylic acid (methyl red) ($pK_a = +4.8$), 4-phenylazo-1-naphthylamine ($pK_a = +4.0$), 4-dimethylaminoazobenzene ($pK_a = +3.3$), 4-aminoazobenzene ($pK_a = +2.8$), 2-amino-5-azotoluene ($pK_a = +2.0$), 4-(phenylazo)diphenylamine ($pK_a = +1.5$), 4-nitroaniline ($pK_a = +1.1$), and {4-[bis(4-dimethylaminophenyl)methylene]-2,5-cyclohexadien-1-ylidene}dimethylammonium (crystal violet) ($pK_a = +0.8$). A 1.0 wt% toluene solution of the indicator (0.3 mL) was added to the treated catalyst (50 mg) suspended in toluene (10 mL), followed by titration of the colored indicator using 0.01 M butylamine in toluene solution.

3. Results and discussion

3.1. Catalytic reaction

The supported tungsten cluster, $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ (**1**)/SiO$_2$, was placed in a glass reaction tube and treated at 300 °C in a helium stream for 1 h. The reaction was initiated by introduction of a methanol solution of cyclohexanone oxime into the helium stream at the same temperature. The reaction profile is plotted in Fig. 1. The catalytic activity decreased with time, probably because of coke formation on the catalyst. Deactivation of various zeolites in the vapor-phase Beckmann rearrangement has been attributed to coke deposition [6,9,10,26]. The selectivi-
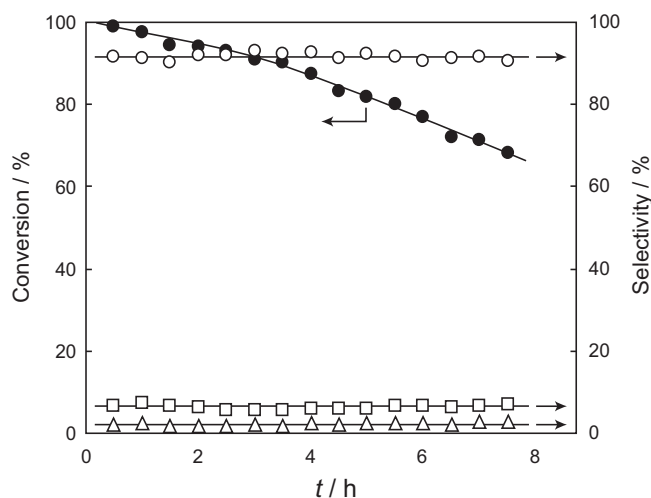

Fig. 1. A typical reaction profile of cyclohexanone oxime catalyzed by $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ (**1**)/SiO$_2$ in a helium stream at 300 °C. Conversion of cyclohexanone oxime (closed circles); selectivity for ε-caprolactam (open circles); selectivity for cyclohexanone and 2-cyclohexen-1-one (open triangles); and selectivity for decomposition products including hexanenitrile and hex-5-enenitrile (open squares).

ties, however, remained steady throughout the reaction. Cluster **1** effectively converted cyclohexanone oxime to ε-caprolactam with 93% selectivity. Cyclohexanone, 2-cyclohexen-1-one, hexanenitrile, and hex-5-enenitrile were formed as by-products, and these by-products are also formed in the Beckmann rearrangement over acidic zeolites [6–8,10,26,27]. The turnover frequency per cluster during a period of 2–4 h was 3069 h^{-1}, assuming that all of the cluster molecules were active. The material balance was 92% at 2–4 h based on the amount of cyclohexanone oxime.

The effect of the reaction temperature on activity and selectivity over **1**/SiO$_2$ at 3 h after the start of the reaction is shown in Fig. 2, where the activation and the reaction were performed at the same temperature. The catalytic activity significantly developed above 250 °C, around which temperature the hydroxo species on the cluster emerged in the thermal treatment of **1** [20]. The selectivity for ε-caprolactam was as high as 85% in the temperature range 250–350 °C. Above 400 °C, selectivity for ε-caprolactam decreased (<22%), and decomposition products such as the nitriles
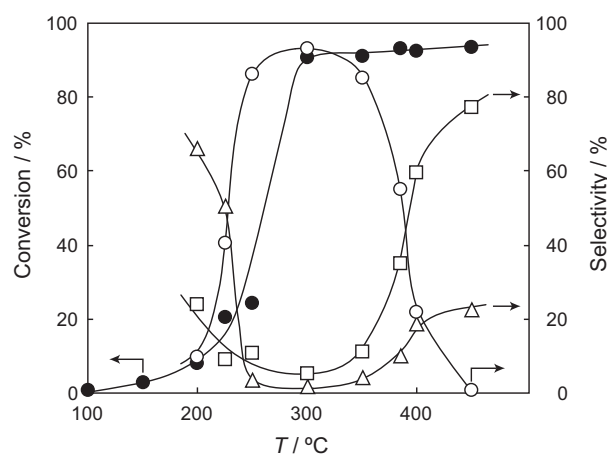
Fig. 2. Temperature effect on the reaction of cyclohexanone oxime over $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ (**1**)/SiO$_2$ in a helium stream at 3 h after the start of the reaction. Conversion of cyclohexanone oxime (closed circles); selectivity for ε-caprolactam (open circles); selectivity for cyclohexanone and 2-cyclohexen-1-one (open triangles); and selectivity for decomposition products including hexanenitrile and hex-5-enenitrile (open squares).

Table 1
Beckmann rearrangement of cyclohexanone oxime over various halide cluster catalysts[a].

Entry	Catalyst	Conversion (%)[b]	Selectivity (%)[c]			
			ε-Caprolactam	Ketones[d]	Nitriles[e]	Others
1	[(Nb$_6$Cl$_{12}$)Cl$_2$(H$_2$O)$_4$]·4H$_2$O/SiO$_2$	32.5	80.8	5.4	6.6	7.2
2	(H$_3$O)$_2$[(Mo$_6$Cl$_8$)Cl$_6$]·6H$_2$O/SiO$_2$	16.0	25.7	21.2	35.3	17.8
3	[(Ta$_6$Cl$_{12}$)Cl$_2$(H$_2$O)$_4$]·4H$_2$O/SiO$_2$	10.0	53.5	19.8	13.5	13.2
4	(H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)/SiO$_2$	90.8	93.1	1.6	2.2	3.1
5	(H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)/SiO$_2$[f]	72.8	88.8	1.4	5.3	4.5
6	(H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)[g]	10.2	22.7	63.9	6.4	7.0
7	(H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)/SiO$_2$[h]	22.5	75.8[i]	10.3[j]	10.1[k]	3.8
8	(H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)/SiO$_2$[l]	67.0	81.3[m]	4.8[n]	8.0[o]	5.9
9	Re$_3$Cl$_9$/SiO$_2$	39.5	9.2	68.2	5.2	17.4
10	W metal	28.7	12.1	79.1	4.2	4.6
11	SiO$_2$	4.1	0.0	72.0	8.1	19.9
12	None	2.9	0.0	68.4	8.5	23.1

[a] After treatment of the catalyst (10 mg) at 300 °C in a helium stream (1.2 L/h), a methanol solution of cyclohexanone oxime (17 mol%, 200 μL/h, 0.65 mmol/h) was added at 300 °C.

[b] Conversion at 3 h after the start of the reaction.

[c] Selectivity at 3 h after the start of the reaction.

[d] Cyclohexanone and 2-cyclohexen-1-one.

[e] Hexanenitrile, hex-5-enenitrile, etc.

[f] In a nitrogen stream (1.2 L/h).

[g] Unsupported crushed crystalline cluster.

[h] A methanol solution of acetone oxime (17 mol%, 186 μL/h, 0.65 mmol/h) was allowed to react.

[i] N-Methylacetamide.

[j] Acetone.

[k] Acetonitrile.

[l] A methanol solution of cyclopentanone oxime (17 mol%, 189 μL/h, 0.65 mmol/h) was allowed to react.

[m] δ-Valerolactam.

[n] Cyclopentanone.

[o] Pentanenitrile, pent-4-enenitrile, etc.

were increased (>60%). A similar increase in the decomposition above 400 °C has been observed in the rearrangement over HY [28] and B-MFI [26]. When **1**/SiO$_2$ was activated at 400 °C and the reaction was performed at 300 °C, the selectivity for ε-caprolactam was 90%. Activation and reaction at 300 °C yielded ε-caprolactam with 92% selectivity, as shown in Fig. 2. These findings indicate that the selectivity depends on the reaction temperature, and that the cluster framework as well as the ligands was retained during the activation at 400 °C.

The catalytic activities of various clusters of Group 5–7 metals and related compounds at 300 °C are listed in Table 1. Supported **1** effectively catalyzed the Beckmann rearrangement of cyclohexanone oxime both under helium and nitrogen streams (entries 4 and 5). Supported clusters of niobium and tantalum were also active catalysts for the reaction (entries 1 and 3). On the other hand, the support (SiO$_2$) and no catalyst had no catalytic activity for the rearrangement (entries 11 and 12), indicating that the

catalytic activities are attributable to the clusters. When tungsten metal was applied to the reaction, the selectivity for the rearrangement was as low as 12% (entry 10). Tungsten hexachloride cannot be used as a catalyst under the reaction conditions, because it melts at 284 °C and boils at 338 °C. From these results, we can conclude that **1** served as a catalyst precursor for the vapor-phase Beckmann rearrangement by taking advantage of its high thermal stability, high melting point, high boiling point, and low vapor pressure.

Table 1 also shows that, when acetone oxime was allowed to react as the starting material over **1**/SiO$_2$, N-methylacetamide was obtained with 76% selectivity (entry 7). Cyclopentanone oxime was also converted to piperidin-2-one (δ-valerolactam) with 81% selectivity over **1**/SiO$_2$ (entry 8). Thus, the halide clusters were effective catalysts for the Beckmann rearrangement of various oximes.

The effect of the solvent, which was used for introduction of the oxime, on activity and selectivity over **1**/SiO$_2$ for the Beckmann rearrangement is shown in Table 2. When protic solvents

Table 2
Effect of solvent on the Beckmann rearrangement of cyclohexanone oxime over (H$_3$O)$_2$[(W$_6$Cl$_8$)Cl$_6$]·6H$_2$O (**1**)/SiO$_2$[a].

Solvent	Conversion (%)		Selectivity (%)[d]			
	(At 0.5 h)[b]	(At 3 h)[c]	ε-Caprolactam	Ketones[e]	Nitriles[f]	Others
Methanol	98.8	90.8	93.1	1.6	2.2	3.1
Ethanol	90.8	80.9	90.5	0.9	4.5	4.1
1-Propanol	83.9	69.0	88.8	1.5	7.9	1.8
Water[g]	57.6	50.4	86.8	1.4	7.9	3.9
Benzene	52.2	6.4	27.5	31.9	22.9	17.7
Toluene	99.2	64.2	27.4	13.6	17.2	41.8
Acetone	97.5	46.0	41.6	17.2	15.8	25.4
Acetonitrile	33.9	10.8	42.1	21.5	23.3	13.1

[a] After treatment of the catalyst (10 mg) at 300 °C in a helium stream (1.2 L/h), a solution of cyclohexanone oxime (17 mol%, 0.65 mmol/h) was added at 300 °C.

[b] Conversion at 0.5 h after the start of the reaction.

[c] Conversion at 3 h after the start of the reaction.

[d] Selectivity at 3 h after the start of the reaction.

[e] Cyclohexanone and 2-cyclohexen-1-one.

[f] Hexanenitrile, hex-5-enenitrile, etc.

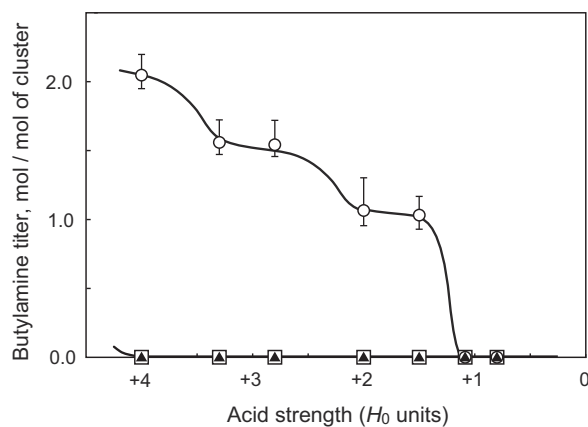[g] An aqueous solution of cyclohexanone oxime (0.40 mol%, 2.4 mL/h, 0.65 mmol/h) was added.

Fig. 3. Butylamine titers *vs.* acid strength for $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$ (**1**)/SiO$_2$, which was treated at 150 °C (open squares) and 300 °C (open circles) in a helium stream. The titer for SiO$_2$ treated at 300 °C (closed triangles) is also shown.

such as methanol, ethanol, 1-propanol, and water were used, the decrease in conversion during the period 0.5–3 h was less than 15%, indicating that the deactivation was slight. The selectivity for ε-caprolactam was high (86%) for these protic solvents. On the other hand, aprotic solvents such as benzene, toluene, acetone, and acetonitrile exhibited a greater decrease in conversion during the period (23–51%), and the selectivity for ε-caprolactam was much lower (27–42%). In the Beckmann rearrangement over various zeolites, alcohol and water solvents are suggested to remove the produced ε-caprolactam from the acid sites before it is converted to coke and other by-products such as nitriles, leading to both prevention of deactivation and high selectivity for ε-caprolactam [6,8,9,26,29,30], which is the case with the halide cluster **1**.

3.2. Catalytic active site

The acid strength of **1**/SiO$_2$ that was activated at 300 °C for 1 h was determined using the butylamine titration method with various Hammett indicators [24,25]. Fig. 3 shows butylamine titers plotted as a function of Hammett acidity value (H_0). The titer for each plot corresponds to the number of acid sites whose acid strength is equal to or weaker than the H_0 value. No acid sites with an H_0 stronger than +4.0 were detected on **1**/SiO$_2$ treated at 150 °C, at which temperature the cluster changed to the aqua cluster $[(W_6Cl_8)Cl_4(H_2O)_2]$ (**2**), as explained by Eq. (1). On the other hand, the cluster activated at 300 °C exhibited an equimolar amount of acid sites at $H_0 \approx 1.5$ with an additional equimolar amount of acid sites at $H_0 \approx 4.0$–2.0. These sites are attributable to the hydroxo ligand, which was developed by the activation above 250 °C, as exemplified by Eq. (2). However, this cluster exhibited no acid sites with an H_0 stronger than +1.1, indicating that the cluster was a weak acid. A molybdenum hydroxo cluster $[(Mo_6Cl_8)Cl_2(OH)_2(H_2O)_2]$ has been reported as a weak acid to afford protons in aqueous solution [31].

Weak acids such as H-beta [7], H-MCM-41, and H-FSM-16 are reported to be effective catalysts for the Beckmann rearrangement [8]; however, HY and H-mordenite, having strong acid sites, exhibit low activity and low selectivity for the reaction [9]. Weak acid sites on Ta$_2$O$_5$/SiO$_2$ and H-USY effectively catalyze the rearrangement, whereas strong acid sites on the catalysts accelerate formation of by-products [4,6]. The rearrangement over HNaY is catalyzed by

weak acid sites with a pK_a less than 1.5, whereas the strong acid sites with a pK_a less than −3.0 are not active for the reaction [5]. Over high-silica MFI, the catalytically active sites are ascribed to nest silanols with very weak acidity, which is undetectable by the temperature-programmed desorption of ammonia (NH$_3$-TPD) [10]. Thus, the weak acid sites ($H_0 \approx$ +1.5) of the hydroxo ligand on the halide clusters are favorable for the selective Beckmann rearrangement.

4. Conclusion

When the tungsten halide cluster, $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$ (**1**), supported on silica gel was activated in a helium stream over the temperature range 250–350 °C, catalytic activity for the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam developed. The maximum selectivity for ε-caprolactam was 93%. The rearrangement of acetone oxime and cyclopentanone oxime was similarly catalyzed by **1**/SiO$_2$. The supported niobium and tantalum clusters activated in the same way also catalyzed the rearrangement of cyclohexanone oxime. Acid titration shows that the activation of **1** developed a weak acid site with $H_0 \approx$ +1.5 for each molecule. Vapor-phase Beckmann rearrangements can be catalyzed by weak solid acids; in contrast, strong acids are less active and less selective for the reaction. Thus, the activated clusters with weak acidity are favorable for the selective Beckmann rearrangement.

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