Promotion of the Electrocatalytic Reduction of Nitrate
Yang, J.

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**Author:** Yang, Jian  
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Formation of volatile products during nitrate reduction on a Sn-modified Pt polycrystalline electrode in acid solution

Abstract
Nitrate reduction is investigated in acid solution on Sn-modified Pt electrodes with different Sn coverages. Volatile products and intermediates were detected by means of on-line electrochemical mass spectroscopy. $\text{N}_2\text{O}$ is found as the main product for intermediate coverages of Sn whereas NO is the dominant product for high Sn coverages. By comparison to $\text{N}_2\text{O}$ reduction on Pt and Sn-modified Pt electrodes with intermediate and high Sn coverages, respectively, $\text{N}_2$ formation is proposed to result from the consecutive reduction of $\text{N}_2\text{O}$ on free Pt sites on PtSn surface. In addition, chemical reactions between ammonia, hydroxylamine and nitrite are also briefly studied as possible reaction steps leading to $\text{N}_2\text{O}$ and $\text{N}_2$ during the nitrate reduction.
2.1. Introduction

Nitrate is widely utilized in fertilizers and pharmaceutics and also discharged from nuclear power plants as waste, having a deteriorating effect on our ecological system and on human health.¹ Catalytic reduction of nitrate has received much attention as one of the most promising ways to solve this problem.² For the removal of nitrate, selectivity of the catalytic process to N₂ is crucial. Moreover, the synthesis of nitrogen compounds from nitrate, such as for instance nitrous oxide, hydroxylamine, and ammonia, which are all industrially significant chemicals, is of interest as well. Especially the selective production of N₂ gas from nitrate reduction is very challenging and progress in this field is currently hampered by a lack of insight into the mechanistic details of the relevant pathways in its formation. Since most of the relevant reactions involved are redox reactions, electrochemistry and electrochemical methods have proven to be extremely useful in investigating the details of the catalytic mechanisms.³

Among the noble metal catalysts studied for nitrate reduction, a great deal of research work has focused on platinum and platinum modified by a second metal, such as germanium, palladium, tin, bismuth, copper, etc.⁴⁻⁹ For the reduction of nitrate on platinum (at low nitrate concentration), the rate-determining step was suggested to be reduction of (adsorbed) nitrate to nitrite; chemisorbed nitric oxide is the key surface intermediate formed from nitrite, and ammonia and hydroxylamine are the main products.¹⁰ However, the electrocatalytic reduction process also depends on other factors such as nitrate concentration and the nature of the supporting electrolyte. At relatively high nitrate concentration and (very) low pH, the indirect reduction of nitrate may take place in the presence of (small amounts of) nitrite, opening up an entirely new nitrate reduction pathway.¹¹ From detailed experiments on single crystal Pt electrodes, it is known that preferential adsorption of hydrogen and anions on specific surface structures greatly influence the nitrate reduction process.¹² However, in general, a recurrent problem is that the reactivity of Pt for the nitrate reduction is low⁸ and that Pt modification by other metals is necessary to enhance both the activity and selectivity. It has been reported that such modifiers are either able to facilitate nitrate adsorption on the surface such that the onset of nitrate reduction shifts to a more positive potential,⁸ or to simply remove strongly adsorbed spectator species, such as anions, from the Pt surface so that nitrate reduction can proceed on a “clean” Pt electrode.⁶ At the same time, it has been observed that the product distribution changes in
accordance with the different character of modifier, although the details of the role of the modifier are still often poorly understood.

Among the various modifiers reported in the literature, Sn is especially interesting as it appears to be one of the very few modifiers that are capable of steering the reduction of nitrate to nitrogen gas with a high selectivity. The group of Shimazu has published a number of papers showing that the reduction of nitrate on Sn-modified Pt (as well as other transition-metal) electrodes yields considerable amounts of $\text{N}_2$,\textsuperscript{7, 13} as detected in the collected gas after several hours of electrolysis. Under somewhat different conditions of a very high cathodic overpotential, a pure Sn electrode was also found to yield the formation of nitrogen gas, with the cathodic corrosion to tin-hydride observed at the same time.\textsuperscript{14, 15} These research results with similar selectivity patterns for $\text{N}_2$ inspired us to investigate the possible mechanism of $\text{N}_2$ formation in nitrate reduction by a Sn-modified Pt electrode.

In this Chapter, we studied the electrocatalytic reduction of nitrate by a Sn-modified Pt electrode at low nitrate concentration. For the electrode preparation, spontaneous deposition is a straightforward method to obtain a submonolayer to monolayer coverage\textsuperscript{16} of a foreign metal on platinum and it has been applied in earlier research on the modification of Pt surface by Sn species for electrocatalysis.\textsuperscript{17} Besides, electrodeposition was applied to achieve various surface coverages, with the aim to compare the product distribution in nitrate reduction at different surface conditions. On-line electrochemistry mass spectroscopy (OLEMS) was applied to follow the volatile products in real time during the electrochemical experiment. In addition, two chemical reactions taking place in solution, i.e. the reaction between $\text{NO}_2^-$ and $\text{NH}_3\text{OH}^+$ and between $\text{NO}_2^-$ and $\text{NH}_4^+$, were also investigated separately under different pH conditions with our mass spectrometry setup, as it was considered that these reactions may play an important role in generating some of the gases observed during the reaction.

2.2. Experimental

All experiments were carried out at room temperature. Before each electrochemical experiment, all glassware was cleaned by a standard procedure as described elsewhere.\textsuperscript{18} NaNO$_3$ (Merck, ACS grade) was first dried at 70 °C overnight and then stored in a vacuum desiccator; SnCl$_2$ (99.99+%, Sigma–Aldrich) was used to modify Pt working electrode; N$_2$O (Messer, purity grade 2.0) was used to study its
electro-reduction properties as intermediate. Ultrapure water (Millipore MilliQ, resistivity > 18.2 MΩ cm) was used to rinse and prepare all electrolyte solutions with Suprapur (Merck) reagents. Prior to the electrochemical measurement, the solution was purged with argon (purity grade 6.0) to remove dissolved oxygen from the electrochemical cell.

A polycrystalline Pt electrode was used in this work. Prior to each measurement, it was flame annealed and subsequently cooled down in an argon atmosphere. After potential cycling in blank solution (0.1M HClO₄) to assure surface cleanliness, the electrode was transferred to another electrochemical cell in which there was a solution of 0.1M HClO₄ + 0.025 mM SnCl₂ for Sn modification. For spontaneous adsorption, the Pt electrode surface was put into contact with the Sn source solution for different time spans (2-15 min); for electrodeposition, a potential more positive than the one for Sn bulk deposition was applied to the electrode for a short time, with Ag/AgCl (KCl, sat) as a reference electrode. For instance, applying 0.23 V (Ag/AgCl) to the working electrode for 10 min would result in a coverage of 0.93. The surface coverage by Sn species was characterized directly through cyclic voltammetry in the potential range of hydrogen adsorption/desorption in the blank solution before measurements in nitrate solution. In all electrochemical experiments, a platinum foil or wire was used as the counter electrode, which was rinsed, flame-annealed and then cooled down in air before each experiment. A reversible hydrogen electrode (RHE) was employed as reference electrode in most experiments unless otherwise stated. Throughout this work, all electrochemical experiments were conducted with an Autolab PGstat20 potentiostat except for the experiments involving on-line electrochemical mass spectrometry, for which an Ivium A06075 potentiostat was employed.

On-line electrochemical mass spectrometry measurements were carried out with an evolution mass spectrometer system (European Spectrometry Systems Ltd.). During measurement, the pressure inside the MS was below 1 × 10⁻⁶ mbar and products at the electrode interface were collected through a small inlet tip positioned close (~10 µm) to the electrode in the electrochemical cell. The tip configuration and pretreatment has been reported in detail in previous papers from our group. The fragmentation ratio of N₂O (m/z = 44) to other important volatile compounds, such as N₂ (m/z = 28), NO (m/z = 30), was measured and calibrated in order to estimate the products that really form on the electrode. In
this work, the fragmentation ratios of N₂O were determined as N₂ : N₂O = 0.0685, and NO : N₂O = 0.202.

The experiments studying the solution-phase chemical reactions between NO⁻ and NH₃OH⁺ and between NO₂⁻ and NH₄⁺ were conducted in the same electrochemical cell as the OLEMS experiments, but without electrodes inside. NaNO₂ (Merck, ACS grade), (NH₃OH)₂SO₄ (Merck, pro analysis) and (NH₄)₂SO₄ (Merck, pro analysis) were used to prepare each 50 ml solutions of 0.2 M concentration respectively. Assuming that dissolved oxygen has a negligible effect on the presumed homogeneous liquid-phase chemical reaction, the appropriate two reactant solutions, which had been freshly prepared, were mixed into spectroelectrochemical cell and so the real concentration during the reaction is for each 0.1 M. Argon bubbling was applied for 2-3 min to stir and mix the solutions at beginning. Hydrochloric acid HCl (pro analysis, 37%) was used to adjust the solution pH, as checked by a Radiometer Copenhagen pH meter during the experiment. The formation of gases, in particular NO, N₂O and N₂, was followed using the tip-based online mass spectrometer.

2.3. Results

2.3.1. Comparison of nitrate reduction on Pt and Sn-modified Pt

In Figure 1 (a), the blank voltammetry of three types of PtSn electrodes is compared to clean platinum: two Pt electrodes modified with Sn generated by the spontaneous deposition method, and a Pt electrode with a large amount of Sn obtained by electrodeposition. In the method of spontaneous deposition, the coverage of Sn species on platinum is sensitively dependent on the concentration of Sn source solution and on the length of time that the Pt electrode had been in contact with Sn source solution. For a 5 min contact time to the Sn source solution, leading to “PtSn(1)”, the hydrogen adsorption region has diminished and an additional cathodic peak appears at around 0.24 V. It has been suggested that Sn deposits onto Pt by a disproportionation to Sn(IV) and Sn_ads on the Pt surface during open circuit. When the contact time was extended to 15 min, the blockage of hydrogen adsorption was more complete and the cathodic peak around 0.24 V has become much smaller: “PtSn(2)”. To obtain a higher amount of Sn on the platinum surface “PtSn(3)” in a relatively short time with low concentration of Sn source solution, electrodeposition turned out to be a better method, although a
high coverage can also be obtained by spontaneous deposition with a longer contact time.

Figure 1. The cyclic voltammograms of the hydrogen region of Pt and 3 Sn-modified Pt electrodes in 0.1 M HClO$_4$ electrolyte (a); and 0.1 M HClO$_4$ / 10 mM NaNO$_3$ electrolyte (b). Scan rate: 50 mV/s. The surface coverage was calculated as (1) 0.266; (2) 0.414; (3) 0.926.

With regard to the valence state of Sn$_{ads}$, electrodeposited tin has been proposed to be in its metallic state for $E < 0.25$ V and in the Sn(II) state for higher potentials, presumably as a mixture of tin oxides (SnO and SnO$_2$). Therefore, in the experiment of nitrate reduction, when the potential of the working electrode is swept in the potential region between 0-0.5 V, the adsorbed Sn may be swept between its metallic and oxidized state. Assuming that in the potential region of hydrogen adsorption, the stoichiometry of hydrogen adsorption per platinum site is 1 and also assuming that there is no measurable hydrogen adsorption on adsorbed Sn, the relative surface coverage of Sn ($\theta_{Sn}$) can be calculated as follows

$$\theta_{Sn} = 1 - \frac{q_{Pt/Sn}}{q_{Pt}}$$

where $q_{Pt}$ is the charge adsorbed in the hydrogen region on a clean Pt electrode, and $q_{Pt/Sn}$ is the same charge on Sn-modified Pt electrode. Using this formula, the electrodes shown in Figure 1 have a $\theta_{Sn}$ equal to 0.266, 0.414, and 0.926,
respectively. Note that Szabo has found that a Sn adatom occupies two H sites on polycrystalline Pt.22

Figure 1(b) illustrates that modification by Sn of Pt can effectively promote the reduction of nitrate. Significantly larger reduction currents are observed in the presence of Sn on the surface, and also the onset potential of nitrate reduction is shifted to more positive potential compared with the clean Pt electrode. These results agree qualitatively with the results reported by Tada and Shimazu7: for the lower coverages, a deactivation is observed for potentials lower than 0.12 V, typically ascribed to the formation of strongly adsorbed hydrogen on platinum, but for the fully covered electrode, no such deactivation is obtained. However, at higher Sn coverages, the electrode is less active for nitrate reduction than at low or intermediate coverage, also in good agreement with the results of Tada and Shimazu.7

2.3.2. Formation of volatile products during voltammetry

Nitrate reduction on polycrystalline Pt electrode does not produce any detectable amount of volatile products, in good agreement with earlier conclusions that the only product of nitrate reduction on pure Pt is ammonia.10 However, when a submonolayer of Sn is present on the Pt surface, volatile nitrogen compounds may be detected as reduction products. For a low coverage of Sn on Pt, N2O is formed as the main and only volatile product (after the necessary corrections for fragmentation), as shown in Figures 2.

Other mass signals measured during the voltammetry, such as NO and N2, were weak enough to consider that the detected NO was a fragment of N2O after ionization by taking into account the accuracy of the fragmentation ratio and the fact that the small ion current corresponding to NO changes with exactly the same trend as the mass signal corresponding to N2O. The trace amount of N2 detected during cyclic voltammetry can be ascribed to the consecutive reduction of nitrous oxide to N2 on the PtSn surface, as will be demonstrated in section 3.3 (although it may also be a fragment of N2O by taking into consideration a small systematic error in the calculated fragmentation ratio). Comparing the potential-dependent mass signal with the current-potential profile, the peak in the ion current corresponding to N2O is at around 0.3 V in the negative-going scan and at 0.25 V in the positive-going scan, whereas the cathodic current does not show a clear peak. At the most negative potential values, all detected ion currents decrease to the background level, suggesting that from ca. 0.3 V other non-volatile products are
formed, presumably mainly hydroxylamine and ammonia, which dominate the product spectrum of nitrate and nitrite reduction at the most negative potentials.\textsuperscript{10}

Figure 2. Mass signals measured during voltammetric potential cycling on a SnW-modified Pt electrode in 10 mM NaNO\textsubscript{3}/0.1 M HClO\textsubscript{4} electrolyte. The electrode was prepared by spontaneous adsorption. Its calculated Sn coverage was about 0.41. Scan rate: 1 mV/s.

Figure 3. Mass signals measured during voltammetric potential cycling on a SnW-modified Pt electrode in 10 mM NaNO\textsubscript{3}/0.1 M HClO\textsubscript{4} electrolyte. The electrode was prepared by UPD, with a calculated coverage of about 0.926. N\textsuperscript{\textasteriskcentered} = \textsuperscript{15}N. Scan rate: 1 mV/s.

When the Pt surface is almost totally covered by Sn species, NO is observed as the main volatile product during the nitrate reduction (see Figure 3). A much
smaller amount of N₂O was detected during the voltammetry and its potential-dependent signal variation is very similar to that of NO. More importantly, the N₂ fragment from N₂O is too weak to be discriminated and there is no other signal attributable to N₂ detected during the process. The small signal at m/z = 14 is in majority a fragment of NO. Also the OLEMS signals at m/z = 31 and 15 are assigned to nitrogen isotope (N*) fragments of NO.

2.3.3 Reduction of N₂O on Sn-modified Pt electrode

Figure 4. The reduction of nitrous oxide on Pt and Sn-modified Pt electrodes in 0.1 M HClO₄ electrolyte: Pt electrode (a); Sn-modified Pt electrodes with the calculated coverage (b) 0.4; (c) 0.92. Scan rate: 1 mV/s.

In order to verify whether N₂O may serve as an intermediate in the formation of N₂ during the nitrate reduction on PtSn electrodes, we studied the voltammetry of N₂O reduction on our Sn-modified Pt electrodes and followed the formation of N₂ (and the consumption of N₂O) with the OLEMS. Figure 4 shows that a pure Pt electrode and a Sn-modified Pt electrode with a low to intermediate Sn coverage are capable of reducing N₂O to N₂, but a Pt electrode with a large amount of Sn does not reduce N₂O and there is no formation of N₂. The cathodic current on Pt electrode modified with high coverage of Sn is very low compared with the other two electrodes, indicating the reduction is sluggish. Furthermore, there is no obvious change in peak potential between pure Pt electrode and one modified with low coverage of Sn. These results are in accordance with earlier work on the influence of Pb, Cd, and Tl adatoms on N₂O reduction on Pt and show that N₂O
reduction only occurs at free Pt sites on the surface. This result implies that during long-term electrolysis experiments, N₂ could be formed from the reduction of N₂O, which is the main volatile product obtained during the nitrate reduction in voltammetry experiments.

2.3.4. Products detected during long-term constant potential experiments

As we demonstrated in the previous section, N₂O reduction occurs within the potential region of 0.1 to 0.3 V on a Pt electrode modified with a small to moderate amount of Sn and the strongest signal for N₂ would be expected at potential of ca. 0.2 V. Therefore, three constant potentials, 0.15 V, 0.2 V and 0.25 V were chosen in a long-term electrolysis experiment and the mass signals corresponding to different products at the different potentials are shown in Figure 5. After correction for mass fragmentation, it is clear that at potential of 0.2 V the ion current of N₂ is larger than at 0.25 V, whereas the reverse is true for N₂O, which strongly suggests that N₂ formation is really from the electrode reaction rather than fragmentation of N₂O gas. Moreover there is good agreement with the experiment of N₂O reduction on the Pt electrode modified with an intermediate coverage of Sn that showed that N₂O reduction achieves a maximum production of N₂ at a potential of 0.2 V.
2.3.5 Chemical reactions

2.3.5.1. Reaction between ammonium and nitrite

It is important to understand and investigate the possible chemical reactions related with nitrite, as nitrite is an intermediate in the electrocatalytic reduction of nitrate. One possible reaction is that between nitrite and ammonium to form N₂ gas as described in:

\[
\text{NO}_2^- + \text{NH}_4^+ \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}
\]  

When pH value is below 5, the nitrite ion exists in equilibria with nitrous acid HONO (HNO₂) and nitrosonium (ON⁺OH₂) in solution. As the acidity increases, the decomposition of HONO occurs much more rapidly and NO gas and nitric acid are formed. As shown in Figure 6(a), when solution pH was adjusted to ca. 1 immediately after the solutions of nitrite and ammonium were mixed together into the cell, defining the beginning of the reaction time, a strong ion current signal corresponding to NO is measured whereas that corresponding to N₂ is about 50 times lower (after correcting for mass fragmentation). Therefore, at this pH, decomposition of HONO dominates the nitrosation reaction so that much more NO is produced than N₂ gas. For comparison, in Figure 6(b) solution pH was adjusted to ca. 3.6 after mixing and then N₂ gas is detected as the dominant gaseous product, with a mass signal that was almost two times larger than the one...
corresponding to NO. However, at higher pH, the N\textsubscript{2} formation reaction is slowed down\textsuperscript{27,28} Therefore, the main product distribution of reaction between nitrite and ammonium is strongly dependent on solution pH. As long as HNO\textsubscript{2} decomposition can be disregarded, N\textsubscript{2} formation may happen from the reaction between nitrite and ammonium. At high pH, say pH=1, which is typical for many electrochemical experiments, HNO\textsubscript{2} decomposition dominates and produces NO.

\textit{2.3.5.2. Reaction between hydroxylammonium and nitrite}

Figure 7. The mass spectrum of N\textsubscript{2}O as main product during reaction between NaNO\textsubscript{2} and (NH\textsubscript{3}OH)\textsubscript{2}SO\textsubscript{4} in solution of pH = 1. Time=0 is the time of mixing the solution and adjusting the pH. The large spikes are due to the formation of bubbles.

The other important chemical reaction associated with nitrite is the reaction between hydroxylammonium and nitrite\textsuperscript{3,29,30} as described by:

\[ \text{NO}_2^- + \text{HONH}_3^+ \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \]  

Figure 7 illustrates that this reaction happens immediately after mixing solutions of nitrite and hydroxylammonium and the solution pH was adjusted to 1. After correcting for fragmentation, there is no other volatile nitrogen species such as N\textsubscript{2} or NO found in the process.

\textbf{2.4. Discussion}

Our results confirm that Sn modification of a Pt electrode has a very significant effect on promoting nitrate reduction on pure Pt electrode. Following Tada and
Shimazu,\textsuperscript{7} we assume that this is related to the enhancement of the rate-
determining step, namely the reaction from nitrate to nitrite:

\[ \text{NO}_3^- + 2 \text{H}^+ + 2 e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \] (3)

The nonlinear dependence of the rate of this reaction on the tin coverage
suggests a Pt-Sn ensemble site as the active site for this reaction.\textsuperscript{7} By comparing the
volatile products of the nitrate reduction at different coverages of the Sn-modified
Pt electrode, we are also able to elucidate the role that Sn plays in the selectivity of
the nitrate reduction. For a low to intermediate coverage, \text{N}_2\text{O} is detected as the
main product. For a high coverage of Sn, NO is detected as the main volatile
product. Under both conditions, \text{N}_2 is at best a minority product. The dependence
of \text{N}_2\text{O} formation on Sn coverage is most likely related with the availability of free
Pt sites. Therefore, we believe that the most likely pathway for \text{N}_2\text{O} formation is
through nitrite/nitrous acid reduction on the bare Pt sites, similar to the
mechanism that we detailed recently for nitrite reduction:\textsuperscript{21}

\[ 2 \text{NO}_2^- + 6 \text{H}^+ + 4 e^- \rightarrow \text{N}_2\text{O} + 3 \text{H}_2\text{O} \] (4)

This reaction is supposed to take place through a surface-adsorbed \text{NO}_{ads}
intermediate.\textsuperscript{3, 21} Simultaneously, free Pt sites are also needed for the consecutive
reduction of \text{N}_2\text{O} to \text{N}_2:

\[ \text{N}_2\text{O} + 2 \text{H}^+ + 2 e^- \rightarrow \text{N}_2 + \text{H}_2\text{O} \] (5)

which we believe is the reaction responsible for the small amount of \text{N}_2 observed
during nitrate reduction on the Sn-modified Pt electrode with a moderate amount
of Sn, and possibly also for the much larger amounts of \text{N}_2 observed in long-term
electrolysis experiments.\textsuperscript{7}

At a high coverage of Sn, gaseous NO is the main volatile product, because
adsorbed NO, which we mentioned is a necessary intermediate in reaction (4), can
no longer bind to the Sn-covered surface. Moreover, at high Sn coverage, the
nitrate reduction takes place at higher overpotentials, and at these potentials nitrite
is reduced to hydroxylamine and ammonia.\textsuperscript{21} This is also the main reason why the
\text{N}_2\text{O} and NO formation decrease at more negative potentials in Figures 2 and 3: the
NO is reducing to other, hydrogen-containing, products at these more reducing
potentials.

We have little direct evidence for the involvement of chemical reactions (1) and
(2) during nitrate reduction on the PtSn electrode. Our experiments indicate that
pH=1, N\textsubscript{2} formation from reaction (1) should be minimal, also because there is little evidence that nitrite and ammonium form simultaneously during the voltammetry, but of course in the long-term electrolysis experiment the importance of this reaction cannot be neglected, as nitrite and ammonium are two important products of the overall nitrate reduction. The reaction between nitrite and hydroxylamine is an important one at pH=1, but at present we cannot assess to what extent it takes place as we have no direct measure for the formation of hydroxylamine. However, hydroxylamine is known to be a main product of nitrite reduction on Pt at more negative potentials. Therefore, the importance of reaction (2) can again not be ruled out during long-term electrolysis experiments. We hope to report on the quantitative formation of hydroxylamine and ammonia at negative potentials in a future publication.

2.5. Conclusions

The Sn-modified Pt electrode can effectively promote the activity for nitrate reduction compared with a pure Pt electrode in acid solution through catalyzing the reduction to nitrite at a PtSn ensemble site. N\textsubscript{2}O is the dominant product on a PtSn electrode with an intermediate coverage of Sn, and likely to be reduced consecutively to N\textsubscript{2} gas on the remaining free Pt sites. We believe that this could be main pathway through which N\textsubscript{2} has been formed in the experiments of Toda and Shimazu. At high Sn coverage, NO\textsubscript{ads} formation is blocked and gaseous NO becomes the main product. There is no direct evidence for the importance of chemical reactions in solution in the formation of N\textsubscript{2} and N\textsubscript{2}O during these voltammetry experiments, but we believe the contributions of such reactions during long-term electrolysis experiments can not be ruled out.

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