

The Combustion of SiCl₄ in Hot O₂/H₂ Flames

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Dedicated to Professor Wolfgang Brockner on the Occasion of his 65th Birthday

Abstract. A simple kinetic model describing the molecular gas phase reactions during the formation of fumed silica (AEROSIL[®]) was developed. The focus was on the formation of molecular SiO₂, starting from SiCl₄, hydrogen and oxygen. Wherever available, kinetic and thermodynamic parameters were taken from the literature. All other parameters are based on quantum chemical calculations. From these data, an adiabatic model for the combustion reaction has been developed. It was found that a significant amount of molecular SiO₂ forms after about 0.1 and 0.6 ms at

starting temperatures between 1000 and 2000 K. The initial reaction of the SiCl₄ combustion in a hydrogen/oxygen flame was found to be different from the combustion in air: The high reactivity of SiCl₄ towards water is favored over the SiCl₄ dissociation, which is the initial and rate-determining step during the combustion of SiCl₄ in air.

Keywords: Fumed silica; AEROSIL[®]; kinetics; density functional calculations

Die Verbrennung von SiCl₄ in heißen O₂/H₂-Flammen

Inhaltsübersicht. Zur Beschreibung der molekularen Reaktionen in der Gasphase während der Herstellung von pyrogenem Siliciumoxid (AEROSIL[®]) wird ein einfaches kinetisches Modell entwickelt. Gegenstand der Arbeiten ist die Bildung von molekularem SiO₂, ausgehend von SiCl₄. Kinetische und thermodynamische Parameter, die in der Literatur nicht zur Verfügung stehen, werden mit Hilfe von quantenmechanischen Methoden berechnet. Im Rah-

men eines adiabatischen Modells für die Verbrennungsreaktion wurde gefunden, dass bei Ausgangstemperaturen von 1000 bis 2000 K ein großer Teil an molekularem SiO₂ gebildet wird. Die Startreaktion in der O₂/H₂-Flamme ist hierbei eine Reaktion von SiCl₄ mit Wasser, anders als bei der Verbrennung von SiCl₄ an Luft, bei der die Dissoziation von SiCl₄ der erste und geschwindigkeitsbestimmende Schritt ist.

Introduction

The formation of silica in a high-temperature combustion process to produce extremely fine particle sized fumed silica or pyrogenic silica is well established as the AEROSIL[®] process. In the past 60 years AEROSIL[®] has gained a broad variety of applications, and the global production capacity of fumed silicas exceeded 100,000 mt. Although the processing of AEROSIL[®] using chlorosilanes as volatile raw materials has been well investigated, very little is known about the basic reactions of this process.

To understand the formation of AEROSIL[®], it is important to know about the underlying molecular mechanisms. Before AEROSIL[®] is formed, a complex combustion process takes place. Actual models of AEROSIL[®] burners assume a spontaneous formation of SiO₂ molecules that will coagulate in order to form particles [1]. The role of molecular SiO₂ and protoparticles is discussed by Sheka [2] resp.

Ulrich [3–7] et al. Since the kinetics of the molecular combustion reaction influences the flame and the temperature field in the reactor, it is necessary to investigate this step in more detail. It is of particular interest, on which time scale the formation of molecular SiO₂ takes place. To make a first step towards this goal, a simple kinetic model was developed.

To our knowledge, there is no kinetic data regarding the combustion of SiCl₄ in a H₂/O₂ flame available in the literature. However, Binnewies et al. [8] state that the reaction of SiCl₄ with water might be an important reaction in this process. On the other hand, Powers found that during the combustion process of SiCl₄ in oxygen, the dissociation of SiCl₄ into SiCl₃ and Cl is the rate determining step [9].

It can be expected that many intermediate species will occur during the combustion process. For instance, Junker et al. detected silaphosgene (O=SiCl₂) when SiCl₄ is brought to reaction with oxygen at high temperatures [10].

In our work, we examined three possible reaction channels for the combustion of SiCl₄ in the H₂/O₂ flame. Kinetic parameters have been computed for several elementary reactions using quantum mechanical methods. In the next step, kinetic models were applied to calculate concentration and temperature as a function of time. To reduce the complexity, an adiabatic system and a plug flow situation in the

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burner was assumed. Therefore, no reactor geometry and flame model were used in our calculations. Furthermore, no coagulation or condensation has been considered, which implies that only the formation of molecular SiO_2 was examined.

Results and Discussion

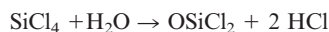
I Selection of elementary reactions

Since the reaction under consideration takes place in a H_2/O_2 flame, we chose the Chemkin model for these reactions as a basis [11]. Additional reactions which include SiCl_4 were selected for our model. As outlined in the introduction, one reaction channel could start with the reaction of SiCl_4 with water, so this reaction was added to our model. Another channel could start with the dissociation of SiCl_4 , since this reaction is important for the combustion of SiCl_4 in oxygen [9]. Besides these reactions, SiCl_4 could react with any of the intermediates occurring during the H_2/O_2 reaction. Since it would have been beyond the scope of this work to include any of these reactions we focused on a reaction of SiCl_4 with OH radicals as a starting point.

Binnewies et al. [8] report chlorosiloxanes as intermediates occurring at temperatures below 1000 K. However, these species are not included in our model, since there is evidence that a particle growth process is less likely under AEROSIL[®] production conditions, where a coagulation process of small protoparticles is assumed [1].

Thus, the following starting reactions of SiCl_4 have been considered:

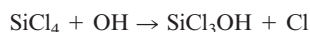
1. Reaction with water



2. Dissociation



3. Reaction with OH radical



II Calculation of kinetic data

The rate constant $k(T)$ of a reaction in the gas phase is

$$k(T) = h/k_{\text{B}} \cdot \exp(-\Delta G^{\ddagger}(T)/RT),$$

where $\Delta G^{\ddagger}(T)$ is the free activation enthalpy, k_{B} the Boltzmann constant, and h the Planck constant.

$\Delta G^{\ddagger}(T)$ has been computed for several elementary reactions using the Dmol3 program [12]. The activation energy, E_{A} , and the Arrhenius factor, A , were obtained by fitting to the Arrhenius equation

$$k(T) = A \cdot \exp(-\Delta E_{\text{A}}/RT).$$

For the bimolecular reactions of SiCl_4 with water and OH radicals, transition states were found and the free activation energy was calculated. For the monomolecular dis-

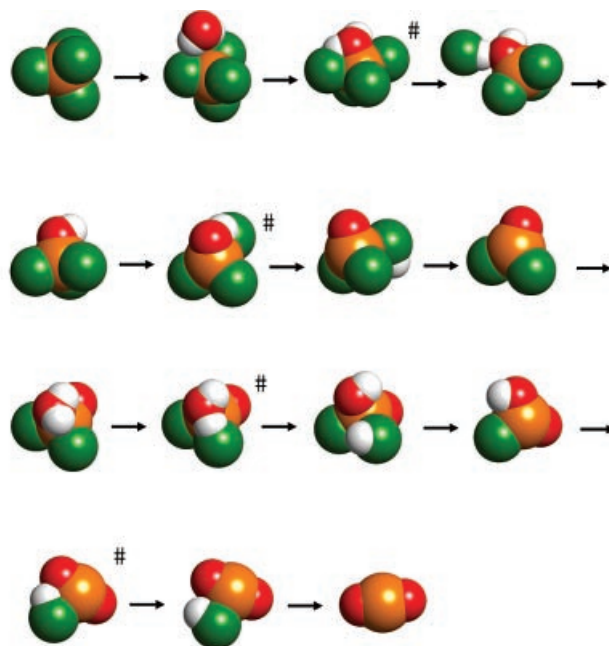


Fig. 1 Reaction of with water. “#” indicates a transition state. (Si: orange, O: red, H: white, Cl: green)

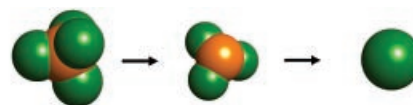


Fig. 2 SiCl_4 dissociation reaction. (Si: orange, Cl: green)

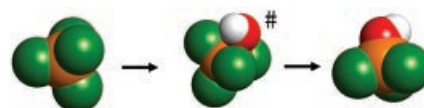


Fig. 3 Reaction of SiCl_4 with OH radical. “#” indicates a transition state. (Si: orange, O: red, H: white, Cl: green)

sociation reaction, only the dissociation energy was calculated and taken as a lower limit for the activation energy. All reaction and activation energies were calculated by the Dmol3 program within the Cerius2 environment [13], using the DNP basis set and the BOP functional [14,15].

The molecular structures for the reactions considered in this work are shown in Figure 1–3. (Structures labeled with “#” are transition states. Some obvious reaction partners are omitted in order to keep the scheme readable.)

The SiCl_4 hydrolysis (Figure 1) takes place in four elementary steps, namely a water/HCl substitution, a HCl elimination, another water/HCl substitution and another

Table 1 Calculated activation energies and Arrhenius factors

Reaction	E_A kJ/mol	A s ⁻¹
SiCl ₄ + H ₂ O → SiCl ₃ OH + HCl	128	8.2·10 ¹¹
SiCl ₃ OH → SiCl ₂ O + HCl	209	2.8·10 ¹³
SiCl ₂ O + H ₂ O → SiClOOH + HCl	70	2.4·10 ¹²
SiClOOH → SiO ₂ + HCl	205	3.7·10 ¹³
SiCl ₄ +OH → SiCl ₃ OH+Cl	188	1.4·10 ⁷
SiCl ₄ → SiCl ₃ + Cl	≅402	–

Table 2 Calculated thermochemical data. A, B, C and D describe the temperature dependency of c_p according to $c_p(T) = A + 10^{-3} \cdot BT + 10^{-5} \cdot CT^{-2} + 10^{-6} \cdot DT^2$.

	$\Delta H^0(298)$ kJ/mol	$\Delta S^0(298)$ J/mol/K	A	B	C	D
SiClOOH	-608	310	74.518	26.545	0	-5.830
SiCl ₂ O	-431	312	72.007	11.196	0	-2.764
SiCl ₃ OH	-785	375	104.681	21.569	0	-4.642

HCl elimination, yielding molecular SiO₂. H₂O and HCl adducts are found as intermediate states.

The kinetic data obtained from the calculations are shown in Table 1. (For the dissociation reaction, the activation energy was estimated from the dissociation energy, labeled with “≅”.)

Experimental data for the activation energy and the Arrhenius parameter exists for the reaction



Powers [9] found $E_A = 401$ kJ/mol and $A = 1.7 \cdot 10^{14}$ s⁻¹ for this elementary reaction. E_A corresponds well to our calculated value.

III Calculation of thermochemical data

To calculate energy balances and temperatures in kinetic simulations, thermochemical data for all species included in the kinetic model is necessary. For all listed molecules except SiClOOH, SiCl₂O and SiCl₃OH data can be found in the NASA database that comes with the kinetics software Kintecus [16]. For the remaining three molecules, quantum mechanical calculations were carried out.

The missing heats of formation were calculated via the hydrides. For the electronic energies, the quantum chemistry software Turbomole [17] was employed, using the RI-MP2/TZVPP//B3LYP/TZVP method. The vibrational contributions to the energy and the heat capacities were calculated using the semi-empirical PM3 method [18].

The calculated heats of formation and standard entropies are listed in Table 2. Junker et al. [10] calculated the heat of formation of SiCl₂O in a similar way, and reported -440 kJ/mol for the heat of formation and 302.4 J for the standard entropy, which is in reasonable agreement with

our calculations. The temperature dependency of heat capacities can be represented in the standard form

$$c_p(T) = A + 10^{-3} \cdot BT + 10^{-5} \cdot CT^{-2} + 10^{-6} \cdot DT^2.$$

Table 2 lists the calculated heat capacities expressed by A, B, C and D.

IV Kinetic modeling

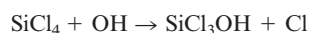
The kinetic modeling was done with the Kintecus software [16]. The activation energies and Arrhenius parameters of the elementary reactions described above as well as the thermodynamic data for all molecules are needed as input for this simulation. Besides the reactions explicitly mentioned above, the elementary reactions of the H₂/O₂ reaction are needed. The Chemkin H₂O model was used for this purpose [11].

Since the reaction



is a rate limiting step in the SiCl₄ oxidation [9], it is assumed that the corresponding reaction channel in our model is at least as slow as this reaction. The experimental kinetic data for this reaction (see above) were used in our model to represent the entire conversion to molecular SiO₂ and HCl.

The Cl atom in the reaction



is, as a simplification, assumed to form HCl immediately under consumption of a hydrogen atom.

With these elementary reactions the following kinetic models were constructed:

Model 1: Pure H₂/O₂ flame. All relevant elementary reactions with H₂ and O₂ are included (Chemkin Model).

Model 2: SiCl₄ in H₂/O₂ flame. All reactions of the Chemkin Model plus all additional elementary reactions listed in this report are included.

Model 3: SiCl₄ in H₂/O₂ flame. All reactions of the Chemkin Model are included plus the elementary reactions of the SiCl₄ hydrolysis.

Model 3 was chosen in order to find out the significance of the SiCl₄ dissociation and the reaction of SiCl₄ with OH.

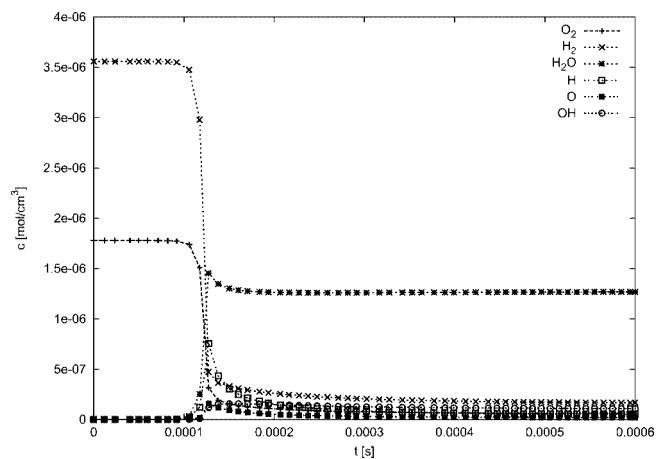
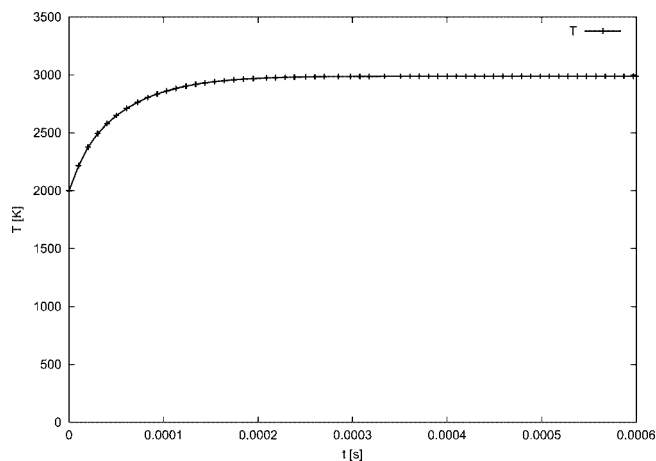
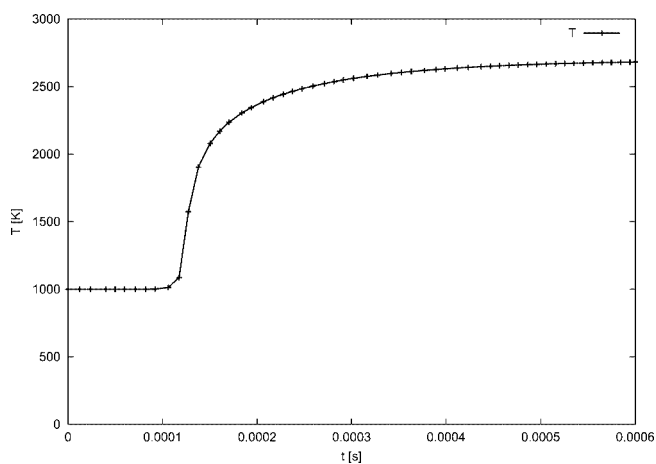
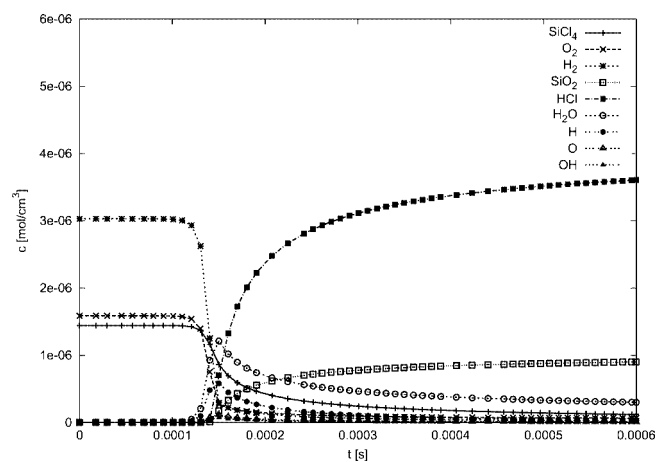
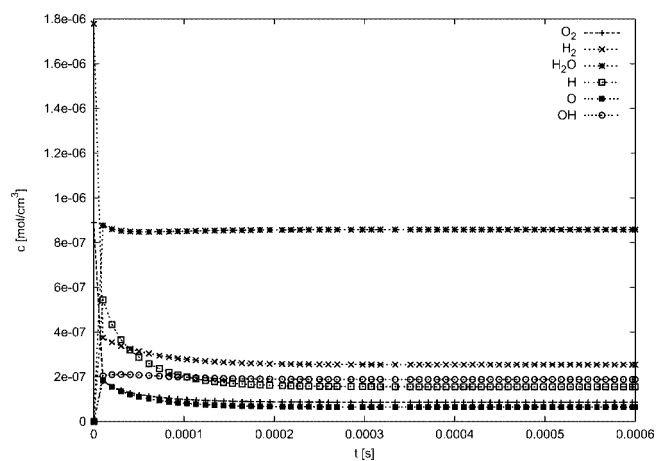
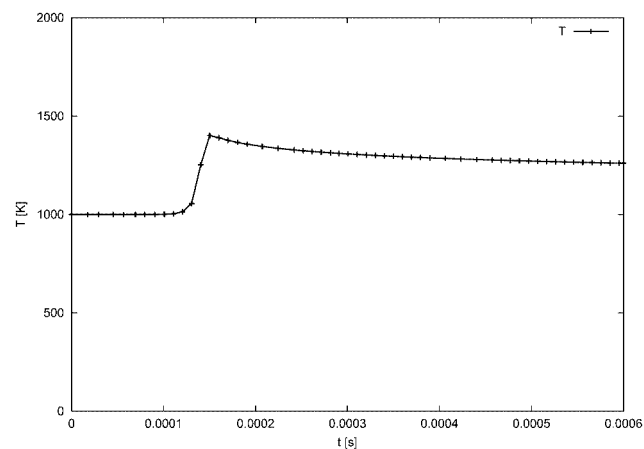
For all three models typical starting concentrations and starting temperatures were chosen. As a simplification, it is assumed that the air consists of 79 % N₂ and 21 % O₂. It has to be mentioned that the adiabatic model is valid only in the local reaction zone on the flame surface. Therefore, the starting temperatures chosen in this work are not necessarily the temperatures of the input gas stream.

The starting conditions for our models are:

Model 1: reactands H₂ + O₂ + N₂; molar ratio (H₂/O₂/N₂) = 2.0/1.0/3.8; $T = 1000$ K and 2000 K; $p = 1$ bar.

Model 2: reactands H₂ + O₂ + N₂ + SiCl₄; molar ratio (SiCl₄/H₂/O₂/N₂) = 1.0/2.1/1.1/4.3; $T = 1000$ K and 2000 K; $p = 1$ bar.

Model 3: same as Model 2.

Fig. 4 Concentration curves for Model 1, $T_{\text{start}} = 1000$ K.Fig. 7 Temperature curve for Model 1, $T_{\text{start}} = 2000$ K.Fig. 5 Temperature curve for Model 1, $T_{\text{start}} = 1000$ K.Fig. 8 Concentration curves for Model 2, $T_{\text{start}} = 1000$ K.Fig. 6 Concentration curves for Model 1, $T_{\text{start}} = 2000$ K.Fig. 9 Temperature curve for Model 2, $T_{\text{start}} = 1000$ K.

The concentration and temperature curves for Models 1 and 2 are shown in Figure 4–7 resp. Figure 8–11 (concentrations in mol/cm^3 , isobaric system, variable volume).

The curves for Model 3 are not shown because there are no visible differences between Model 2 and 3. Model 3 was

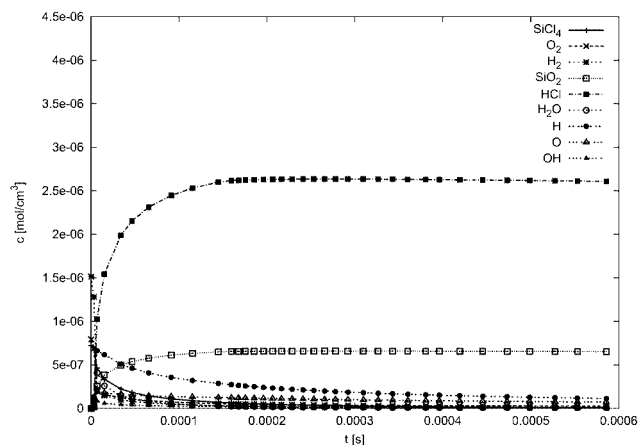


Fig. 10 Concentration curves for Model 2, $T_{\text{start}} = 2000$ K.

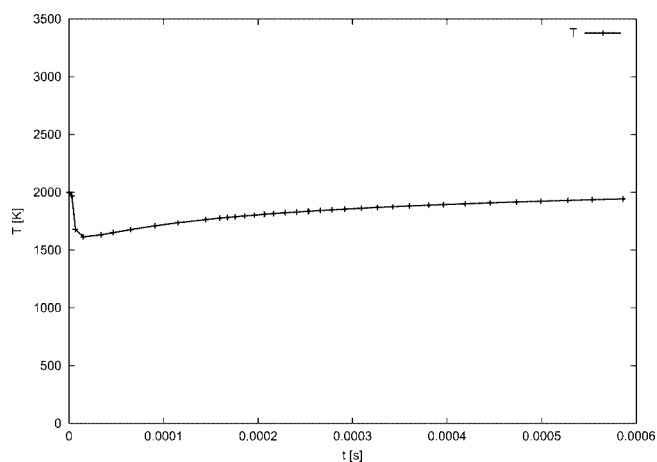
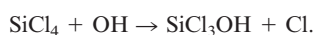


Fig. 11 Temperature curve for Model 2, $T_{\text{start}} = 2000$ K.

included to examine the difference between including and neglecting the reaction channels



and



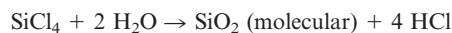
We conclude from the results that these channels do not have an impact on the overall reaction and the reaction of SiCl₄ with water appears to be the most important reaction path in our model. It can be further concluded that the dissociation of SiCl₄ is, unlike during the combustion in oxygen, not the rate limiting step in the H₂/O₂ flame due to the much higher reactivity of SiCl₄ towards water.

It is roughly estimated from the results shown in Figure 8 and 10 that the main amount of molecular SiO₂ is formed after about 0.1 to 0.6 ms depending on the starting temperature, when choosing starting temperatures between 1000 K and 2000 K.

The temperature curves of the SiCl₄ combustion are different from the ones of the pure H₂/O₂ reaction. Starting at 1000 K, T first increases in a similar way as in the H₂/O₂

reaction, but then energy consumption causes a temperature decline. Starting at 2000 K, at the beginning a slight temperature decline is found, followed by a continuous increase of temperature.

The net reaction



is endothermic (about +470 kJ/mol) and consumes energy stemming from the H₂/O₂ reaction. The reaction enthalpy for the total reaction



is $\Delta H^{298} \cong -12$ kJ/mol. As stated above, the formation of solid AEROSIL[®] is not included in the model. This process is exothermic and will have a further impact on the temperature in the flame.

The model described in this article revealed details of the molecular reactions taking place in the AEROSIL[®] flame. It can serve as a basis for further investigations. To obtain more quantitative information, several extensions are possible. To extend the kinetic model, further elementary reactions could be investigated and included. Validation of the kinetics could be done with experimental measurements. For unimolecular reactions the RRKM method should be considered to obtain more quantitative results.

Computational accuracy could be increased by using high-level ab initio methods such as Coupled Cluster or multireference methods. These methods, however, are computationally demanding. Finally, the results of the kinetic modeling could be used in combination with CFD flame models and particle growth models [1].

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