

1 **A compact skeletal mechanism for *n*-dodecane with optimized semi-global low-temperature**  
2 **chemistry for diesel engine simulations**

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15  
16 **Abstract:** A skeletal mechanism with 54 species and 269 reactions was developed to predict  
17 pyrolysis and oxidation of *n*-dodecane as a diesel fuel surrogate involving both high-temperature  
18 (high-T) and low-temperature (low-T) conditions. The skeletal mechanism was developed from a  
19 semi-detailed mechanism developed at the University of Southern California (USC). Species and  
20 reactions for high-T pyrolysis and oxidation of C<sub>5</sub>-C<sub>12</sub> were reduced by using reaction flow analysis,  
21 isomer lumping, and then merged into a skeletal C<sub>0</sub>-C<sub>4</sub> core to form a high-T sub-mechanism.  
22 Species and lumped semi-global reactions for low-T chemistry were then added to the high-T sub-  
23 mechanism and a 54-species skeletal mechanism is obtained. The rate parameters of the low-T  
24 reactions were tuned against a detailed mechanism by the Lawrence Livermore National Laboratory  
25 (LLNL), as well as the Spray A flame experimental data, to improve the prediction of ignition delay  
26 at low-T conditions, while the high-T chemistry remains unchanged. The skeletal mechanism was

1 validated for auto-ignition, perfect stirred reactors (PSR), flow reactors and laminar premixed  
2 flames over a wide range of flame conditions. The skeletal mechanism was then employed to  
3 simulate three-dimensional turbulent spray flames at compression ignition engine conditions and  
4 validated against experimental data from the Engine Combustion Network (ECN).

5 **Keywords:** *n*-dodecane; surrogate; spray flames; ignition delay; skeletal mechanism

## 7 **1. Introduction**

8 Accurate prediction of diesel engine combustion requires realistic chemical kinetics. However, diesel  
9 fuels consist of a large number of components and involve an even larger number of intermediate species  
10 and reactions during the combustion process, and thus it is difficult to employ fully detailed mechanisms  
11 in practical engine simulations as the computational cost would be intractable. As a simplification, surrogate  
12 mixtures with one or a few components have been developed to mimic the physicochemical behaviors of  
13 the real diesel fuels [1]. For instance, *n*-dodecane features a molecular size close to that of average diesel  
14 components, and has been employed recently as a surrogate fuel to model diesel fuel combustion [2-12].  
15 Detailed mechanisms for large hydrocarbons, e.g. *n*-dodecane, can consist of thousands of species and  
16 reactions when low temperature (low-T) chemistry is involved [13-17]. For instance, the detailed  
17 mechanism developed by Westbrook et al. [14] for *n*-alkanes from *n*-octane to *n*-hexadecane consists of  
18 2775 species and 11,173 reactions. Such large mechanisms need to be reduced for computationally tractable  
19 three-dimensional (3-D) simulations.

20 Mechanism reduction has been extensively studied in the last few decades and a number of reduction  
21 methodologies have been brought up [18]. Reduced mechanisms can be obtained by removing unimportant  
22 species and reactions from the detailed mechanisms and lumping of similar species and reactions, using  
23 such methods as reaction flow analysis (RFA) [19], sensitivity analysis [20-22], principal component  
24 analysis (PCA) [23], detailed reduction [24], directed relation graph (DRG) [25-28] and variants[29-31],  
25 path flux analysis (PFA) [32] and isomer-lumping [33,34]. However, reduced mechanisms for practical  
26 engine fuels with low-T chemistry obtained by such methods may still be large [2,35]. For example, a

1 skeletal mechanism for *n*-dodecane developed by Luo *et al.* [2] consists of 106 species and 420 reactions.  
2 The mechanism was developed using DRG with expert knowledge (DRGX) [36] and DRGASA [30] based  
3 on a detailed LLNL mechanism [13]. This mechanism and its variants [7, 8] have been coupled to different  
4 turbulent combustion models in Spray A flame simulations [5,7-11] and compared with the experimental  
5 data from the Engine Combustion Network (ECN). Narayanaswamy *et al.* [37] reduced the detailed LLNL  
6 mechanism to a skeletal *n*-dodecane mechanism with 255 species and 2289 reactions through multi-stage  
7 reduction strategy involving DRGEP [29] and chemical lumping [33]. The reduced mechanism was  
8 implemented in a tabulated-chemistry combustion model by Ayyapureddi *et al.* [38] to simulate the Spray  
9 A flames. D’Errico *et al.* [39] developed a reduced mechanism of *n*-dodecane using a reduction algorithm  
10 combining sensitivity and flux analysis starting from a much smaller detailed mechanism that consists of  
11 435 species and 13,532 reactions. This mechanism was also used to simulate the Spray A flames for  
12 validation under engine-relevant conditions. These mechanisms are still relatively large and can be  
13 expensive for engine simulations, especially when the mechanisms are coupled to advanced combustion  
14 models [5, 7, 9,10], or high-fidelity LES studies [11]. More importantly, all of these reduced mechanisms  
15 show increased errors in low ambient temperature conditions for Spray A flames, and thus a compact and  
16 more accurate mechanism is needed for engine simulations.

17 In the present work, multiple reduction methods, including RFA and isomer-lumping, will be employed  
18 to obtain a skeletal mechanism for *n*-dodecane based on a semi-detailed mechanism developed by You *et*  
19 *al.* [40]. The semi-detailed mechanism consists of 171 species and 1306 reactions and has been widely  
20 validated, which is a good candidate to start with. Semi-global reactions for low-T chemistry are merged to  
21 the skeletal mechanism and subsequently optimized to better predict the negative temperature coefficient  
22 (NTC) behavior. The final mechanism consists of 54 species and 269 reactions in the skeletal form and is  
23 validated against detailed mechanisms and available experimental data. The mechanism is further tuned for  
24 and applied in 3-D lifted diesel spray flame simulations.

## 1 **2. Mechanism development**

### 2 *2.1 Skeletal mechanism development*

3 For a range of conditions in ignition and combustion, the kinetics of fuel decomposition to smaller  
4 fragments, which is described by C<sub>5</sub>-C<sub>12</sub> sub-mechanism, is always fast and can be decoupled from the  
5 oxidation kinetics of the H<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> fragments [40]. In the development of the skeletal mechanism, the  
6 C<sub>5</sub>-C<sub>12</sub> sub-mechanism from a detailed mechanism is firstly simplified by eliminating unimportant species  
7 and reactions, and isomer lumping is also employed. The simplified C<sub>5</sub>-C<sub>12</sub> sub-mechanism is then merged  
8 into the simplified H<sub>2</sub>/CO/C<sub>1</sub>-C<sub>4</sub> base mechanism. Lumped low-T reactions are then added and tuned,  
9 resulting in an optimized skeletal mechanism with 54 species and 269 reactions. The reduction and tuning  
10 procedure is further discussed in the following.

11 The detailed C<sub>5</sub>-C<sub>12</sub> mechanism developed by You *et al.* [40] consists of 60 species and 522 reactions.  
12 In the present study, reduction is based on data sampled from homogeneous, adiabatic, isobaric reactors.  
13 The parameter range covers pressure of 1–80 bar, equivalence ratio of 0.5–2.0, and initial temperature of  
14 800–1600 K. RFA is first employed to quantify the contribution of each reaction to the generation and  
15 consumption of each species. Analysis is conducted from the reactant n-dodecane as the starting point.  
16 Reaction pathways that are not important to the consumption of n-dodecane are removed along with the  
17 species that the path leads to. Species associated with reaction pathways contributing e.g. 95% of the total  
18 consumption of n-dodecane are retained. This reduction is performed successively until all the retaining  
19 C<sub>5</sub>-C<sub>12</sub> species find their main pathways to translate into C<sub>1</sub>-C<sub>4</sub> fragments. By further applying radical  
20 isomers equilibrium assumptions [34], isomers of n-dodecyl and other alkyls are lumped to three and one  
21 representatives, respectively. The reduced C<sub>5</sub>-C<sub>12</sub> sub-mechanism obtained after performing species and  
22 reactions elimination and isomer lumping consists of 18 species and 60 reactions. It is worth noting that  
23 fuel cracking process goes fast during the oxidation of n-dodecane and many intermediates are in steady  
24 state, only the main reaction pathways that are important for the decomposition of n-dodecane to fragments  
25 are needed to reproduce this process.

1 In order to obtain a compact C<sub>0</sub>-C<sub>4</sub> sub-mechanism, the C<sub>0</sub>-C<sub>4</sub> core in a reduced high-T mechanism for  
2 *n*-dodecane oxidation in Vie *et al.* [41] is adopted. This core is reduced from USC-MECH II (111 species  
3 and 784 reactions) [42] for high temperature oxidation (high-T). Two species, namely C<sub>4</sub>H<sub>7</sub> and pC<sub>4</sub>H<sub>9</sub>, and  
4 the involved reactions are added to accommodate the C<sub>5</sub>-C<sub>12</sub> sub-mechanism and more accurately predict  
5 the C<sub>4</sub> species concentrations in pyrolysis, which was not considered by Vie *et al.* [41], resulting in a new  
6 C<sub>0</sub>-C<sub>4</sub> core with 32 species and 191 reactions.

7 In the end, a semi-global scheme involving 4 species and 18 reactions for low-T chemistry of *n*-decane  
8 developed by Bikas and Peters [43] is modified to be suitable for *n*-dodecane and appended to the skeletal  
9 mechanism to capture the NTC behavior. Transition between low and high temperatures showing the  
10 negative temperature dependence can be well reproduced by applying the Low-T sub-mechanism with  
11 lumped reaction steps, which is rather efficient for practical engine simulations [43] and has been fully  
12 investigated for *n*-heptane in [44, 45]. A 54-species skeletal mechanism (SK54a) is thereby obtained, which  
13 can be found in the supplementary material.

#### 14 2.2 Need for further tuning

15 The ignition delay time of SK54a is compared with experimental measurement by Vasu *et al.* [46] and  
16 detailed mechanisms [13, 40] in Fig. 1. Simulations were performed under constant-pressure, adiabatic  
17 conditions by the Senkin program package [47]. It is seen that the ignition delay time at low-T (~700 K) is  
18 significantly over-predicted by the You *et al.* mechanism [40] and SK54a while predictions by the LLNL  
19 [13] show improved agreement with experimental data.

20 3-D simulations of Spray A flames are further performed by a three-dimensional computational fluid  
21 dynamics code CONVERGE with the flame condition listed in Table 1. The simulation setup has been  
22 reported in our previous studies [9, 48] and will be briefly described here. The Reynolds-averaged Navier-  
23 Stokes (RANS) method is used along with the Re-normalization Group (RNG) k- $\epsilon$  turbulence model [49].  
24 The traditional Lagrangian-Eulerian method is employed, where the liquid phase is treated as Lagrangian  
25 discrete parcels and the gas-phase is solved on a Eulerian mesh. Source terms are used to exchange mass,  
26 momentum, and energy between the two-phases. The “blob” injection method [50] is used with the Kelvin-

1 Helmholtz and Rayleigh-Taylor (KH-RT) model [51, 52] for primary and droplet secondary breakup. A  
2 dynamic drag model [53] was used to account for the droplet drag. Droplet evaporation is modeled using  
3 the Frossling correlation [54]. The gas phase reaction is modeled by a delta function combustion model  
4 [55]. The computational region is a cube with dimension of 108 mm in each direction. Adaptive mesh  
5 refinement (AMR) is employed to refine the mesh. The minimum cell size is 0.25 mm with peak cell counts  
6 in the order of one million. Based on a previous study, this resolution is deemed to be grid convergent for  
7 RANS calculations [56]. Lift-off length (LOL) and ignition delay data measured under a wide range of  
8 ambient conditions are used for validation of the developed n-dodecane skeletal mechanism. The conditions  
9 involve ambient gas temperature of 800-1100 K, fuel injection pressure of 150 MPa, ambient oxygen  
10 concentration of ( $X_{O_2}$ ) 15%, ambient gas density of 22.8 Kg/m<sup>3</sup>. Ignition delay obtained using SK54a and  
11 the previous 106-species mechanism (SK106) [2] are compared with the ECN data [57-59] in Fig. 2 for  
12 different ambient temperatures. It is seen that the predictions at 1100 K and 1000 K are better for the SK54a  
13 mechanism, showing an advantage of SK54a at high temperatures. At 800 K, SK54a however significantly  
14 over-predicts the ignition delay (which is longer than 6 ms and not shown here), showing the need for  
15 further tuning of the semi-global low-T reactions.

### 16 *2.3 Mechanism Tuning*

17 Mechanism tuning is conducted against the detailed LLNL mechanism in auto-ignition. Although there  
18 are uncertainties in the detailed mechanism as well but at least with this approach the tuned mechanism will  
19 match a published detailed one, wherever experimental data is rare and more scattered. Simulations are  
20 performed under representative conditions of pressure  $p = 20$  bar, initial temperature  $T_0 = 800$  K and various  
21 equivalence ratios as shown in Fig. 3. It is seen that the ignition delay time is over-predicted by SK54a at  
22 lean conditions, while better agreement is observed for rich mixtures. As a result, ignition delay in Spray A  
23 flames predicted using SK54a at  $T = 800$  K is expected to be longer than that of SK106 which is reduced  
24 from LLNL.

25 Sensitivity analysis is then performed using SK54a at  $p = 20$  bar,  $\phi = 0.5, 1.0, 2.0$ , and  $T_0 = 800$  K in  
26 the NTC regime to identify the reactions important for low-T ignition. Sensitivity Coefficients (SC) are

1 defined as the resulting percentage change in the ignition delay time ( $\tau$ ) by doubling the rate constant of the  
2  $i$ th reaction,  $k_i$  [60].

$$3 \quad SC_i = \frac{\tau(2k_i) - \tau(k_i)}{\tau(k_i)}$$

4 Eight reactions with the largest SC are selected and summarized in Fig. 4. Reactions with positive SC  
5 decelerate ignition and make ignition delays longer, and those with negative SC accelerate ignition and  
6 result in shorter ignition delays. Sensitivity analysis is also performed under other engine relevant  
7 conditions, for example  $p = 50$  bar and 80 bar, which shows the same tendency as in  $p = 20$  bar and is not  
8 showing here.

9 It can be seen from Fig. 4 that ignition delay times under fuel rich conditions ( $\phi = 2.0$ ) have larger  
10 sensitivity to Low-T reactions (R3, R4, R5) than lean conditions ( $\phi = 0.5$ ), which makes it impossible to  
11 change ignition delay time at lean conditions without affecting rich conditions by tuning these reactions.  
12 R1, R2, R6, R7 and R8 are involved in the high-T sub-mechanism and cannot be changed. Then we  
13 observed that R1 is more sensitive for lean conditions, for the formation of vinoxy radical ( $\text{CH}_2\text{CHO}$ )  
14 facilitates the chain branching of the overall reactivity and the facilitation is more inclined in lean conditions  
15 than rich conditions [60]. Although R1 cannot be tuned for its significant influence to high temperature  
16 oxidation, decomposition reaction of ketohydroperoxide  $\text{OC}_{12}\text{H}_{23}\text{OOH}$  (R9) can be tuned to accelerate  
17  $\text{CH}_2\text{CHO}$  formation which leads to small species through one step reaction ( $\text{OC}_{12}\text{H}_{23}\text{OOH} \rightarrow$   
18  $\text{CH}_2\text{O} + 3\text{C}_2\text{H}_4 + \text{C}_2\text{H}_5 + \text{C}_2\text{H}_3\text{CHO} + \text{OH}$ ). As the products of R9 are appointed arbitrarily with reference to  
19 Bikas and Peters [43], the  $\text{OC}_{12}\text{H}_{23}\text{OOH}$  decomposition reaction is changed to the following formation:  
20  $\text{OC}_{12}\text{H}_{23}\text{OOH} \rightarrow 3\text{C}_2\text{H}_4 + \text{C}_2\text{H}_5 + 2\text{CH}_2\text{CHO} + \text{OH}$ , to produce vinoxy radicals ( $\text{CH}_2\text{CHO}$ ) that can facilitate  
21 the chain branching of low temperature reactivity. And the rate constant of this reaction is tuned down by  
22 a factor of two to accommodate the new mechanism, resulting in SK54b mechanism, which can be found  
23 in the supplementary material. Performance of SK54b can be seen in Fig. 3, which shows improvement  
24 after the above tuning.

1 The tuned mechanism (SK54b) was then employed in 3-D Spray A flame simulations, and predictions  
2 of ignition delay time are shown in Fig. 5. Over-prediction of ignition delay by ~25% is still observed at  
3 the 800 K ambient temperature, which is also observed with SK106 in Fig.2. Since the first stage ignition  
4 was found to occur in the lean mixtures and the main ignition in rich mixture [11], ignition delay of rich  
5 cases (e.g.,  $\phi = 2.0$ ) at 800 K is further tuned down by ~25% using another round of reaction tuning based  
6 on sensitivity analysis, resulting in a final mechanism (SK54).

7 The second round of sensitivity analysis is performed using SK54b to identify important low-T  
8 reactions that are sensitive to ignition delay times at  $p = 20$  bar,  $\phi = 0.5, 1.0, 2.0$  and  $T_0 = 800$  K, 900 K.  
9 Selected reactions with high sensitivities are shown in Fig. 6. It can be seen that R2 mostly facilitates  
10 ignition in all investigated cases with negative sensitivity coefficient. And R6 accelerates ignition of fuel  
11 rich condition and decelerates ignition of fuel lean condition at  $T_0 = 800$  K, which however has little  
12 influence on ignition delay time at  $T_0 = 900$  K. Therefore, tuning up rate constants of R2 and R6 will result  
13 in a further decrease of ignition delay time at  $\phi = 2.0, T_0 = 800$  K and ignition delay times at  $T_0 = 900$  K and  
14  $\phi = 0.5, T = 800$  K nearly unaffected. The tuning of these two reactions (R2 and R6) is conducted through  
15 careful trial and error, leading to the final mechanism (SK54), which can be found in the supplementary  
16 material. Performance of SK54 after this round of tuning can be found in Fig. 5. Improvement achieved can  
17 be seen here that ignition delay time at  $T_0 = 800$  K can be better reproduced by SK54.

### 18 **3. Mechanism Validation**

#### 19 *3.1 Validation for elementary reactors and flames*

20 The mechanism is first validated for shock tube ignition delay data [46,61] at various pressures and  
21 equivalence ratios. Fig. 7 shows comparison between experimental data and predicted ignition delay for  
22 pressure of 20 bar and 50 bar, and various equivalence ratios. It is seen that the present mechanism agrees  
23 well with the experimental data, and the overall discrepancy is smaller than that using the detailed LLNL  
24 mechanism due to the tuning of low-T chemistry. It is therefore expected that the auto-ignition delay of



1 homogeneous mixtures can be more accurately captured for flames that fall within the above parameter  
2 range, which is relevant to the Spray A flame conditions.

3 To further verify the performance of the mechanisms, especially the simplified C<sub>5</sub>-C<sub>12</sub> fuel cracking  
4 sub-mechanism, pyrolysis of *n*-dodecane in stirred reactors [62] and flow reactors [63] was simulated with  
5 the present mechanism and compared with the experimental data by Herbinet *et al.* [64] and Dahm *et al.*  
6 [65]. Fig. 8 shows the comparison of the *n*-dodecane conversion rate calculated with different mechanisms  
7 [13, 40] in comparison with experimental data. Species profiles during the pyrolysis processes are further  
8 compared in Figs. 9-10. It is seen that the reduced mechanism shows overall similar accuracy in the different  
9 pyrolysis cases to that of the more detailed You *et al.* mechanism, for these two mechanisms share the high  
10 temperature chemistry, while the LLNL mechanism shows overall larger discrepancies.

11 Figure 11 shows extended validations of the laminar flame speed of *n*-dodecane/air mixtures during  
12 one-dimensional (1-D) flame simulations [66] evaluated using SK54 and You *et al.* mechanism [40], in  
13 comparison with experimental data in literature [67-69]. Agreement between SK54 and You *et al.*  
14 mechanism is of the order of the scatter of the experimental data at various conditions of pressures, inlet  
15 temperatures and equivalence ratios. This is expected since the flame speed is primarily controlled by high  
16 temperature chemistry, while You *et al.* mechanism and SK54 share the high temperature C<sub>0</sub>-C<sub>4</sub> core, which  
17 has been extensively validated against flame speed data, although some discrepancy exists for the  
18 simplification. Also, the present skeletal mechanism is primarily developed for simulations of diesel engine  
19 relevant conditions for which absolutely accurate prediction of laminar flame speed is not so necessary [2].

### 20 3.2 Validation for 3-D spray flame simulations

21 The newly developed skeletal mechanism SK54 is further applied to simulate spray flames. The  
22 simulation results are compared with experimental data performed under compression-ignition (CI) engine  
23 conditions from the ECN [57,70-72]. The experimental and computational configurations are shown in  
24 Table 1. Details of the 3D simulations are described in section 2.2.

1 Figure 12 shows the comparison of experimental data and predicted ignition delay and LOL at fuel  
2 injection pressure of 150 MPa, ambient oxygen concentration of ( $X_{O_2}$ ) 15%, ambient gas density of 22.8  
3  $Kg/m^3$  and various ambient temperatures. It is seen from Fig. 12a that the ignition delays are well  
4 reproduced at high temperatures ( $T > 1000$  K), indicating the high fidelity of the high-T sub-mechanism in  
5 the skeletal mechanism. Some discrepancies are observed at low-T conditions wherein ignition delays are  
6 under-predicted at ambient temperatures of 900 K and 850 K, and slightly over-predicted at 800 K. The  
7 differences may be due to the simplification of the lumped low-T oxidation sub-mechanism. It is noted that  
8 the prediction at 800 K is within the experimental uncertainty range. The LOL comparison is reported in  
9 Fig. 12b. It is seen that the present mechanism accurately reproduces the experimental LOL data at both  
10 low and high temperature conditions. Overall, the predictions of the present mechanism are reasonably  
11 good compared to the measurements for the wide range of ambient temperatures investigated.

12 Figures 13 and 14 show the comparisons of ignition delay and LOL between the experimental data and  
13 predictions at ambient gas temperature of 900 K, ambient gas density of 22.8  $Kg/m^3$ , different fuel injection  
14 pressures and ambient oxygen concentrations. Overall, the simulations capture the experimental trends well.  
15 As the present mechanism under-predicts ignition delay at the condition  $T=900$  K, all cases in Fig. 13a  
16 show about 10-20% shorter ignition delay time compared to the experimental data. Similar observation is  
17 made in Fig. 14a also at different oxygen concentrations. However, the predictions of LOL presented in  
18 Figs. 13b and 14b are in good agreement with experiments.

19 Comparisons of ignition delay and LOL at ambient gas temperature of 900 K, fuel injection pressure  
20 of 150 MPa, ambient oxygen concentration of ( $X_{O_2}$ ) 15% and different ambient densities are shown in Fig.  
21 15. Again, the ignition delay is under-predicted with larger discrepancies at lower ambient densities.  
22 Overall, the ignition delay and LOL at these ambient densities are reasonably reproduced by the skeletal  
23 kinetic mechanism.

#### 24 **4. Conclusions**

1 A compact skeletal mechanism with 54 species and 269 reactions was developed for *n*-dodecane using  
2 a hybrid and decoupling approach. The high temperature C<sub>5</sub>-C<sub>12</sub> mechanism module is firstly simplified  
3 from the detailed mechanism of You *et al.* [40] by eliminating unimportant species and reactions and isomer  
4 lumping, guided by RFA. The C<sub>5</sub>-C<sub>12</sub> sub-mechanism is then merged to a reduced C<sub>0</sub>-C<sub>4</sub> core based on the  
5 USC-Mech II [42]. Semi-global reactions for NTC chemistry are added and tuned against the detailed  
6 LLNL mechanism and experimental data to eventually obtain a 54-species skeletal mechanism.

7 The tuned mechanism was validated against experimental data for shock tubes, stirred reactors, flow  
8 reactors, and laminar flame speed, and compared with other mechanisms. It is shown that the skeletal  
9 mechanism performs well over a wide range of parameters in elementary flame experiments. Furthermore,  
10 the skeletal mechanism was applied for 3-D Spray A flame simulations. Comparison with experimental  
11 data obtained from the ECN shows that the ignition delay and flame LOL are reasonably well reproduced  
12 by the tuned skeletal mechanism under various conditions, thus providing a valid option for efficient and  
13 accurate multi-dimensional engine combustion simulations.

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## 5 **6. Supplementary material**

6 Supplementary data including newly developed mechanisms (SK54a, SK54b, SK54) associated with  
7 this article can be accessed on online.

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