

**PHOTOCHEMICAL DECOMPOSITION OF 1,2,3,4-TETRAHYDRO-1-NAPHTHYL HYDROPEROXIDE. PHOTOCATALYTIC EFFECTS OF 3d TRANSITION METAL 2,4-PENTANEDIONATES**

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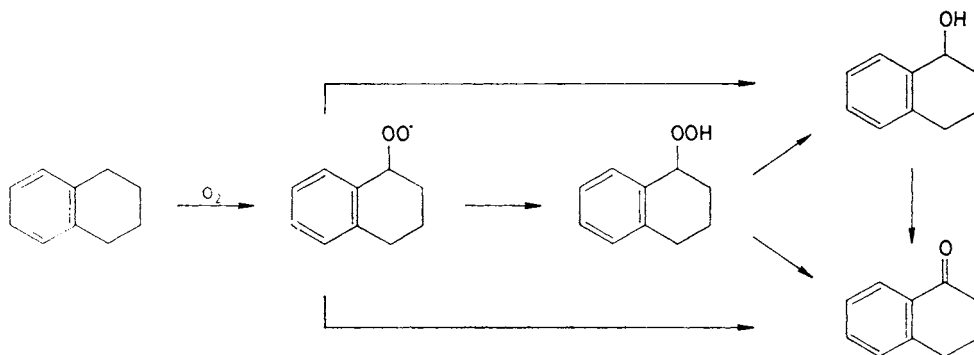
The photochemical decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (THP) in benzene has been investigated. The kinetics of the formation of the main products and of the removal of THP have been measured. It has been demonstrated that the solvent participates in the overall mechanism of THP photolysis. The effects of Fe(III), Co(III), Co(II), Mn(III), Cu(II), Cr(III) and Ni(II) 2,4-pentanedionates on the kinetics of THP photolysis and the formation of the main products have been investigated. Fe(III) and Co(III) 2,4-pentanedionates act as catalysts of the photochemical decomposition of THP.

The decomposition of organic hydroperoxides catalyzed by transition metal complexes has been studied extensively for a number of years, especially in connection with the oxidation of organic substrates by dioxygen<sup>1,2</sup>. Most of these studies present new kinetic data and propose reaction schemes for these processes, but no general relationships between the structure and the properties of the metal complexes on the one hand and their catalytic activity on the other have as yet been established. Resolution of this problem would be of considerable importance not only for the chemical industry processes, it would also give a clue to the elucidation of important theoretical questions concerning, for example, oxidation processes in living organisms.

In recent years, there have been studies dealing with the effect of radiation on the catalytic activity of metal complexes in various model and real systems<sup>3,4</sup>. Even though good quality experimental data are extremely difficult to obtain and the available results are mostly of qualitative character, these studies are those which may go a long way towards elucidating the relations between the chemical properties of metal complexes and their catalytic activity.

The thermal decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (THP) has been investigated as a liquid-phase, homogeneously catalyzed reaction, mostly in connection with the oxidation of 1,2,3,4-tetrahydronaphthalene<sup>5,6</sup>. The main products isolated were 1,2,3,4-tetrahydronaphthol (TOL) and 1,2,3,4-tetrahydro-1-oxonaphthalene (TON). The mechanism proposed<sup>7</sup> for this reaction is outlined in Scheme 1.

The photochemical decomposition of THP, on the other hand, has received very little attention<sup>8</sup>.



SCHEME 1

The aim of the present work was to study the chemical changes of THP induced by UV-VIS radiation and the effect of the radiation on the catalytic activity of 3d transition metal 2,4-pentanedionates during the photochemical decomposition of THP.

## EXPERIMENTAL

### Chemicals

1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide was prepared by the oxidation of 1,2,3,4-tetrahydronaphthalene by dioxygen<sup>9</sup>. 1,2,3,4-Tetrahydro-1-naphthol was prepared by the reduction of THP by sodium sulphite<sup>10</sup>, and 1,2-dihydronaphthalene was obtained by dehydration of 1,2,3,4-tetrahydro-1-naphthol<sup>10</sup>. 1,2,3,4-Tetrahydro-1-oxonaphthalene was a commercial product (Fluka). Co(II), Co(III), Mn(III), Cr(III), Ni(II) and Cu(II) 2,4-pentanedionates were prepared according to published procedures<sup>11-16</sup>.  $[Fe(acac)_3]$  (acac denotes 2,4-pentanedionate) was obtained commercially (Merck). Commercial benzene of analytical grade (Lachema) was used as received. The chemicals employed for analyses were of analytical grade.

### Procedure

The decomposition of THP was carried out in a thermostatted double-jacket glass photochemical reactor of c. 200 ml volume with magnetic stirring. An RVL-X 125 W medium-pressure mercury lamp (main emission lines at 303 nm, 313 nm, 365 nm, 404 nm, and 436 nm) was located at the centre of the reactor, in a water-cooled glass ring. The reaction space was connected to a gas burette. The reactor was designed to permit measurement of the reaction space temperature and sampling without escape of the protective atmosphere. The reactor was made of Pyrex glass which removed from the polychromatic radiation wavelengths  $< 300$  nm. The absorption spectrum of a  $1 \cdot 10^{-2}$  mol  $dm^{-3}$  solution of THP in benzene indicated that in the above described

reactor the solution absorbed only photons of wavelengths within the range 300–320 nm. The addition of 3d transition metal 2,4-pentanedionates markedly enhanced the absorption of radiation at wavelengths  $>320$  nm. The bulk of the photons absorbed from the radiation of the RVL-X lamp was of a wavelength of 365 nm and for  $[\text{Fe}(\text{acac})_3]$  also 436 nm. Most experiments were carried out using 100 ml of c.  $1 \cdot 10^{-2}$  mol  $\text{dm}^{-3}$  solution of THP in benzene at 303 K. The concentration of added transition metal 2,4-pentanedionate was always  $1 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ . The oxidation of THP was prevented by a protective atmosphere of nitrogen above the reaction solution. Comparative measurements of catalyzed and uncatalyzed thermal decomposition of THP were made in the same reactor and under the same conditions as described above. The quantum yields were measured in a thermostatted quartz vessel placed in a dark box. The reaction vessel was vigorously shaken. The source of the exciting radiation was a HBO 200 high-pressure mercury lamp placed in an air-cooled jacket equipped with quartz optics. Interference filters (Carl Zeiss, Jena) were used to isolate wavelengths of 300 or 365 nm. The intensity of the incident radiation was measured by means of ferrioxalate actinometer<sup>17</sup>.

#### Analytical Methods

The decrease in THP concentration was followed by iodometric titration<sup>9</sup>. The reaction mixture composition was determined using a CHROM IV gas chromatograph (1.2 m column, 5% Carbowax 20 M, Inerton AW, 110–160°C). Prior to the g.c. analysis, unreacted THP was converted to TOL by reaction with triphenylphosphine<sup>18</sup>. The reaction products were also identified by thin-layer chromatography (Silufol UV 254,  $\text{CHCl}_3 : \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 = 10 : 1$ ). Chemical changes of  $[\text{Co}(\text{acac})_3]$  were detected by a method described in the literature<sup>19</sup>. Absorption spectra were recorded on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena).

## RESULTS AND DISCUSSION

### *Photolysis of 1,2,3,4-Tetrahydro-1-Naphthyl Hydroperoxide*

The effect of radiation emitted by a medium-pressure mercury lamp on a benzene solution of THP was investigated under the above experimental conditions. The rate of removal of THP was followed and the reaction products were analyzed. The major reaction products were TOL and TON, in a ratio, TOL : TON = 5 : 1, which remained nearly constant over the whole period of observation. Other products, found in concentrations an order of magnitude lower, were phenol and 1,2-dihydronaphthalene, the latter being apparently formed by dehydration of TOL. Phenol is probably formed *via* interaction between the solvent and the hydroxyl radicals generated in THP photolysis. In addition, small amounts of naphthalene and 1,2,3,4-tetrahydronaphthalene were identified qualitatively. No gaseous products were detected during the photolysis of THP. The variations in the concentrations of THP and most of the products in the reaction mixture as functions of time are shown in Fig. 1.

In addition, the thermal decomposition of THP was followed under comparable conditions. At 303 K, no decrease in the initial concentration of THP was observed over a period of several hours.

*Effect of 3d Transition Metal 2,4-Pentanedionates  
on the Photolysis of 1,2,3,4-Tetrahydro-1-Naphthyl Hydroperoxide*

The effects of Co(II), Co(III), Fe(III), Mn(III), Cu(II), Cr(III) and Ni(II) 2,4-pentanedionates on the rate of the photochemical decomposition of THP and on the amounts of the various products in the reaction mixture were investigated, special attention being paid to the relative amounts of TOL and TON. The above complexes were chosen for the following reasons: *a*) they are well-defined compounds; *b*) on account of the flexibility of the ligand, its complexes with a number of central ions are similar in character; *c*) they have good solubility in organic solvents; *d*) extensive data on the photochemistry of these complexes are available which show that the central metal ion is usually reduced on exposure to radiation<sup>20</sup>.

In order to be able to compare the catalytic activities of the complexes for the photochemical decomposition of THP, we first determined their catalytic activities in the thermal decomposition under comparable conditions at 303 K. Co(II), Mn(III), Cu(II) and Ni(II) 2,4-pentanedionates were found to be catalytically active. For the other complexes, no decrease in the concentration of THP was observed over a period of 120 min. The results obtained are presented in Table I.

On addition of transition metal 2,4-pentanedionates there are marked changes in the UV-VIS absorption spectra of benzene solutions. For a  $1 \cdot 10^{-1} \text{ mol dm}^{-3}$  solution of THP in benzene containing  $1 \cdot 10^{-3} \text{ mol dm}^{-3}$   $[\text{Co}(\text{acac})_3]$  or  $[\text{Fe}(\text{acac})_3]$ , 84 or 91% of the incident radiation of wavelength 300 nm is absorbed, respectively. Radiation at 365 nm is completely absorbed by these complexes. Thus, if the addition

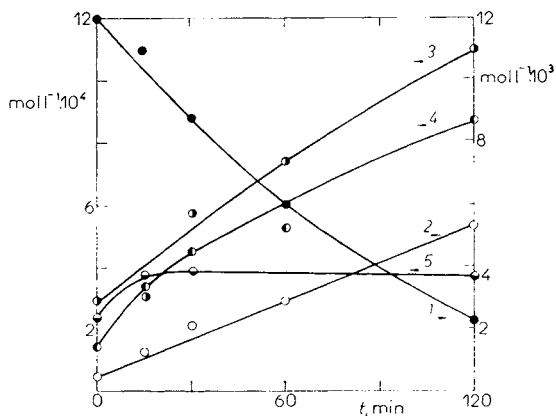


FIG. 1

Products of the photochemical decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide.  $[\text{THP}] = 1 \cdot 2 \cdot 10^{-3} \text{ mol dm}^{-3}$  in benzene;  $T = 303 \text{ K}$ ;  $[\text{N}_2]$ ; no catalyst; 1 THP; 2 TOL; 3 TON; 4 phenol; 5 1,2-dihydronaphthalene

of a 2,4-pentanedionate enhances the photochemical decomposition of THP, this effect must originate in a sensitizing or a photocatalytic action of the complex. The kinetics of the photochemical decomposition of THP in the presence of Fe(III), Co(II), Co(III), Cr(III) and Mn(III) 2,4-pentanedionates are shown in Fig. 2. Of the total reaction time of 240 min, the first 60 min was allowed for the thermal decomposition of THP, a further 120 min for the photochemical reaction, and finally 60 min again for the thermal reaction. This procedure gives a clear view of the effect of radiation on the decomposition of THP and may also provide information on the mechanism by which radiation affects the course of the reaction<sup>21</sup>. As can be seen from Fig. 2, Fe(III) and Co(III) 2,4-pentanedionates have the largest effects on the photochemical decomposition of THP. These complexes do not accelerate the thermal reaction and only on irradiation does the THP decomposition begin to occur. On termination of irradiation, the decomposition of THP is rapidly decelerated or even stopped. However, this experimental fact does not exclude either the sensitization mechanism or the photocatalytic effect of the complexes.

An important information on the mechanism is also provided by the quantum yield of a photochemical reaction. When  $\Phi > 1$ , the sensitization mechanism can be definitely excluded. From Table II the quantum yields of the photochemical decomposition of THP are seen to be much lower than unity and therefore are not useful in deciding between the possible mechanisms of THP photolysis. On the basis of literature data<sup>19,20,22</sup> it can be assumed that exposure to thermal energy and radiation results in the reduction of  $[\text{Fe}(\text{acac})_3]$  and  $[\text{Co}(\text{acac})_3]$  to the Fe(II) and Co(II) complexes. Experiments have established that, when the photolysis of THP is complete, the reaction solution contains 50% of Co(III) ions and 16% of

TABLE I

Effect of transition metal 2,4-pentanedionates on the composition of products from thermal decomposition of THP.  $[\text{THP}] = 1.3 \cdot 10^{-2} \text{ mol dm}^{-3}$  in benzene;  $[\text{M}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ;  $[\text{N}_2]$ ;  $T = 303 \text{ K}$

Catalyst	TOL $\text{mol dm}^{-3}$ $\cdot 10^3$	TON $\text{mol dm}^{-3}$ $\cdot 10^3$	$\frac{\text{TOL}}{\text{TON}}$	THP conversion <sup>d</sup> %
$[\text{Co}(\text{acac})_2]$	5.37 <sup>a</sup>	5.41 <sup>a</sup>	1	10.2
$[\text{Ni}(\text{acac})_2]$	2.99 <sup>b</sup>	0.38 <sup>b</sup>	7.9	16.9
$[\text{Cu}(\text{acac})_2]$	4.32 <sup>a</sup>	1.87 <sup>a</sup>	2.3	14.4
$[\text{Mn}(\text{acac})_3]$	2.58 <sup>c</sup>	0.74 <sup>c</sup>	3.5	7.3

<sup>a,b,c</sup> Concentrations determined at THP conversions of >90%, 47% and 41%, respectively;  
<sup>d</sup> after 120 min.

Co(II) ions, and c. 33% of Co(II) is present in an insoluble form. Fig. 2 demonstrates that the  $[\text{Co}(\text{acac})_2]$  is a catalyst of the thermal decomposition of THP. No such experiments have been made for the iron complex, but we assume that the photochemically generated  $[\text{Fe}(\text{acac})_2]$  is also catalytically active in the thermal reaction. The mechanism of the photocatalytic effect of  $[\text{Co}(\text{acac})_3]$  and  $[\text{Fe}(\text{acac})_3]$  on the photolysis of THP may lie in photochemical reduction of the central Fe(III) and Co(III) atoms to form complexes which catalyze the thermal decomposition of THP.  $[\text{Co}(\text{acac})_2]$  and  $[\text{Mn}(\text{acac})_3]$  are catalytically active in the thermal decomposition of THP and their effect in increasing the rate of the photolysis of THP is unimportant. As indicated by literature data, there is competition between the photochemical reduction of  $[\text{Mn}(\text{acac})_3]$  and the thermal reaction even at room temperature<sup>20</sup>, and this may explain the catalytic activity of this complex in the thermal decomposi-

TABLE II

Quantum yields of the photochemical decomposition of THP on 120 min irradiation by a HBO 200 lamp.  $[\text{THP}] = 1 \cdot 10^{-1} \text{ mol dm}^{-3}$ ;  $[\text{M}(\text{acac})_n] = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$

Catalyst	$\Phi$ (THP molecules/ $h\nu$ )	
	300 nm	365 nm
0	0.02	0
$[\text{Fe}(\text{acac})_3]$	0.06	0.19
$[\text{Co}(\text{acac})_3]$	0.20	0.18

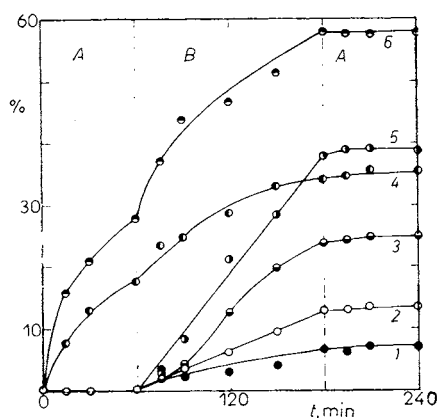


FIG. 2

Catalyzed thermal (A) and photochemical (B) decompositions (% conversion) of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide.  $[\text{THP}] = 1.35 \cdot 10^{-2} \text{ mol dm}^{-3}$  in benzene;  $[\text{M}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$ ;  $T = 303 \text{ K}$ ;  $[\text{N}_2]$ ; 1  $[\text{Cr}(\text{acac})_3]$ ; 2 no catalyst; 3  $[\text{Co}(\text{acac})_3]$ ; 4  $[\text{Mn}(\text{acac})_3]$ ; 5  $[\text{Fe}(\text{acac})_3]$ ; 6  $[\text{Co}(\text{acac})_2]$

tion of THP. The addition of Cr(III), Cu(II) or Ni(II) 2,4-pentanedionate, on the other hand, causes a decrease in the rate of the photochemical decomposition of THP relative to the rate of the uncatalyzed reaction. The kinetics of the photolysis of THP in the presence of  $[\text{Cr}(\text{acac})_3]$  are shown in Fig. 2. The decrease in the rate of THP photolysis in the presence of these poorly catalytically active complexes is most likely to be due to their high absorbances in the region where THP absorbs as well.

The transition metal 2,4-pentanedionates affect not only the rate of THP photolysis but also the relative amounts of the products, especially TOL and TON (Table III). The presence of  $[\text{Mn}(\text{acac})_3]$  leads to the formation of TOL as virtually the only product, while the presence of  $[\text{Fe}(\text{acac})_3]$  markedly enhances the production of TON. In all the cases, phenol was found among the photolysis products. Its formation suggests that the photolysis of THP occurs by a free radical mechanism.

In assigning a mechanism to the photolysis of THP in the presence of metal ions, consideration must be given to a couple of equations frequently quoted in the literature for the reaction between a metal of unstable oxidation state and an organic or inorganic hydroperoxide<sup>22</sup>.

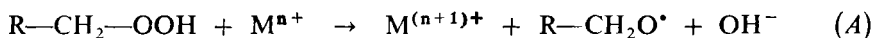


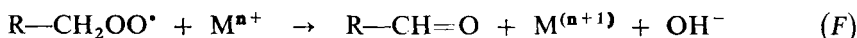
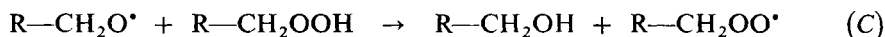
TABLE III

Effect of transition metal 2,4-pentanedionates on the composition of products from photoinitiated decomposition of THP.  $[\text{THP}] = 1.3 \cdot 10^{-2} \text{ mol dm}^{-3}$  in benzene;  $[\text{M}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ;  $[\text{N}_2]$ ;  $T = 303 \text{ K}$ ; molar absorption coefficients,  $\epsilon$ , at 313 nm; an RVL-X 125 W lamp

Catalyst	$\log \epsilon$	TOL <sup>a</sup> $\text{mol dm}^{-3} \cdot 10^3$	TON <sup>a</sup> $\text{mol dm}^{-3} \cdot 10^3$	Phenol $\text{mol dm}^{-3} \cdot 10^3$	$\frac{\text{TOL}}{\text{TON}}$	THP conversion <sup>d</sup> %
$[\text{Mn}(\text{acac})_3]$	3.9	9.8	0.7	1.0	14.9	74.1
$[\text{Cr}(\text{acac})_3]$	4.0	6.1	0.9	0.4	6.5	31.2
$[\text{Ni}(\text{acac})_2]$	3.7	8.0 <sup>b</sup>	1.3 <sup>b</sup>	0.5 <sup>b</sup>	6.1	42.2
0	—	5.3 <sup>c</sup>	1.1 <sup>c</sup>	0.9 <sup>c</sup>	4.8	48.8
$[\text{Co}(\text{acac})_2]$	3.8	6.3	1.5	0.8	4.2	80.6
$[\text{Co}(\text{acac})_3]$	3.9	6.7	1.7	0.8	4.0	89.2
$[\text{Cu}(\text{acac})_2]$	4.2	5.3	1.9	0.7	2.8	44.2
$[\text{Fe}(\text{acac})_3]$	3.6	7.4	3.1	0.9	2.0	83.2

<sup>a,b,c</sup> Concentrations determined at THP conversions of >90%, 89% and 71%, respectively; <sup>d</sup> after 120 min.

The results obtained indicate that the reaction of THP with a transition metal ion takes place predominantly according to equation (A). The reduction of the transition metal ion by interaction with THP seems to occur very slowly under the experimental conditions used in the present work. The initiation step in the photolysis is the photochemical reduction of the metal ion in its higher oxidation state, followed by interaction of this ion with THP according to equation (A). The subsequent process may be assumed to occur by classical free radical mechanism for the decomposition of THP with the participation of the solvent<sup>7</sup>.



SH = benzene

It is interesting to note that  $[\text{Fe}(\text{acac})_3]$  and  $[\text{Co}(\text{acac})_3]$ , which have been found to be photocatalytically active in the decomposition of THP, also show photocatalytic effects in the photochemical oxidation of 1,2,3,4-tetrahydronaphthalene by dioxygen<sup>23</sup>.

#### REFERENCES

1. Kamiya Y., Beaton S., Lafortune A., Ingold K. U.: *Can. J. Chem.* **41**, 2020 (1963).
2. Csányi L. J., Sáky K., Hollósi K.: *Oxid. Commun.* **6** (1-4) 199 (1984).
3. Onkubo K., Arikawa Y., Sakaki S.: *J. Mol. Catal.* **26**, 139 (1984).
4. Luňák S., Sedlák P., Vepřek-Šiška J.: *React. Kinet. Catal. Lett.* **26** (1-2) 39 (1984).
5. Yamada T., Kamiya Y.: *Bull. Chem. Soc. Jpn.* **51**, 830 (1978).
6. Yamada T., Kamiya Y.: *Bull. Chem. Soc. Jpn.* **52**, 474 (1979).
7. Mizukami F., Imamura J.: *Bull. Chem. Soc. Jpn.* **51**, 1404 (1978).
8. Ueberreiter K., Brun W.: *Makromol. Chem.* **68**, 24 (1968).
9. Swern D.: *Org. Synth.* **34**, 90.
10. Chizkevskaya M., Idelchik Z. B.: *Zh. Obshch. Khim.* **27**, 83 (1957).
11. Ellern J. B., Ragsdale R. O.: *Inorg. Synth.* **11**, 84 (1969).
12. Bryant B. E., Fernelius W. C.: *Inorg. Synth.* **5**, 188 (1957).
13. Charles R. G.: *Inorg. Synth.* **7**, 183 (1963).
14. Fernelius W. C., Blanch J. E.: *Inorg. Synth.* **5**, 130 (1957).
15. Gach F.: *Monatsch. Chem.* **21**, 98 (1900).
16. Moore T. S., Young M. W.: *J. Chem. Soc.* **1932**, 2694.
17. Hatchard C. G., Parker C. A.: *Proc. R. Soc. London A* **325**, 518, (1956).
18. Horner L., Jurgeleit W.: *Justus Liebig's Ann.* **591**, 138 (1955).
19. Vasvári G., Hajdu I. P., Gál D.: *J. Chem. Soc., Dalton Trans.* **1974**, 465.



20. Lintvedt R. L. in the book: *Concepts of Inorganic Photochemistry* (A. W. Adamson and P. D. Fleischauer, Eds), Part 7, p. 269. Wiley, New York 1975.
21. Luňák S., Vašková M., Vepřek-Šiška J.: *Z. Naturforsch.* 38b, 1293 (1983).
22. Filipescu N., Hla Way: *Inorg. Chem.* 8, 1863 (1969).
23. Luňák S., Vašková M., Vepřek-Šiška J.: This Journal, in press.

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