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# Graphical abstract

## Insights into biphasic oxidations with hydrogen peroxide; towards scaling up

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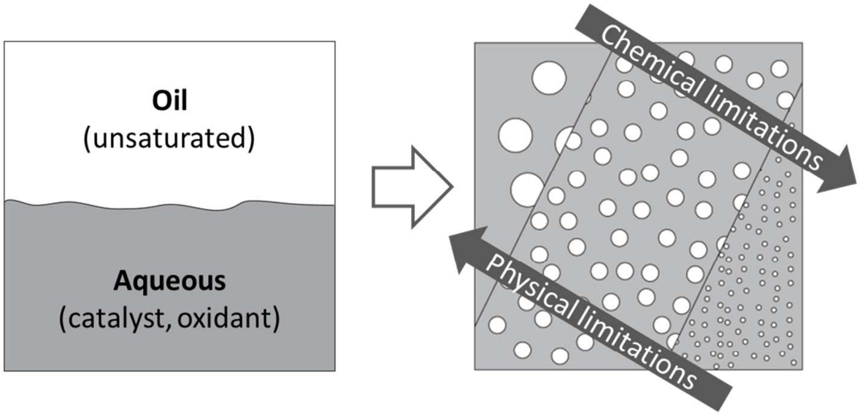

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**ARTICLE TYPE**

# Insights into biphasic oxidations with hydrogen peroxide; towards scaling up

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Bi-phasic oxidations using hydrogen peroxide oxidant and a tungsten-based catalyst (e.g. $Na_2WO_4$) can proceed quickly and effectively without the need for organic solvents or added phase transfer agents in emulsified systems. Providing sufficient contact area between phases easily overcomes the physical limitations associated with the phase transfer of species, facilitating its scale-up, recyclability of the catalyst and easing product separation. Using the epoxidation of sunflower seed oil as a model reaction, we have also shown how the chemical and safety limitations associated with the parallel decomposition of hydrogen peroxide by $Na_2WO_4$ can be supressed by the use of readily available water soluble organic carboxylic acids and careful consideration of the catalyst to acid ratio. The combination of chemical and engineering solutions with a near 100% hydrogen peroxide yield, makes, for the first time, this green oxidation pathway attractive for large-scale industrial applications.

## Introduction

The oxidation of organic molecules is a fundamental transformation in a wide range of industrial chemical processes,[1,2] including in the formation of value-added intermediates.[3] There is a need to move away from the traditional methods of oxidation, which often require the use of stoichiometric levels of oxidants such as chromates, permanganates and periodates, which may lead to complex heat management requirements and/or produce by-products that are harmful to the environment.[1] Cleaner, selective processes using more benign oxidants such as air,[4,5] oxygen,[6] or hydrogen peroxide[7] are preferred. Hydrogen peroxide is often considered to be a green oxidant[8] due to its high oxygen content and benign water by-product, although the synthesis of hydrogen peroxide still requires attention.

Many tungstate-based catalytic systems have been reported to be active for oxidation reactions with aqueous hydrogen peroxide solutions.[9,10] In many cases the substrates to be oxidised are not water miscible and bi-phasic systems are used to avoid the use of organic solvents. Potential catalyst transfer limitations in such systems can be overcome by the use of phase transfer agents, as demonstrated in a number of exemplars using oily alkenes.[11,12] A number of these phase transfer agents have been introduced as counterions to the active catalyst species,[13,14,15,16] or incorporated directly into the catalytic molecule via ligation,[17,18] to ease the transfer of catalytic species between organic and aqueous phases.[19] An important example of such a system is described by Noyori and co-workers; based on a sodium tungstate catalyst and a halide-free phase transfer agent (methyltrioctylammonium hydrogensulfate), oxidation proceeds without the need for organic solvents.[11] In the absence of phase transfer agents, negligible conversions are achieved.

An alternative to this chemical approach to overcome mass transfer limitations in bi-phasic systems is to focus instead on the physical problem of interfacial area. Control of the mutual interface can be achieved using dispersive systems, in particular by defining the size of droplets of one of the phases in the other through emulsification. This technique has been used in a range of organic-aqueous reactions,[20,21] however, careful assessment of how the interfacial area affects the reaction rate remains poorly described in most cases.

Moreover, despite hydrogen peroxide being a relatively cheap commodity, the economic feasibility of these green oxidation processes relies on achieving a hydrogen peroxide atom efficiency close to its theoretical maximum of 47 %, where one O atom per $H_2O_2$ molecule is incorporated in the final oxidised product.[22] In many cases, this efficiency is severely compromised by $H_2O_2$ decomposition into $O_2$ and $H_2O$, with obvious associated safety issues when conducted at scale. Clearly, cautious evaluation and quantification of the peroxide efficiency is of paramount importance if tungstate/$H_2O_2$ aqueous systems are to be used in large-scale industrial applications.

In this paper, using the system schematically illustrated in Figure 1, we demonstrate that in-depth understanding of the effect of reaction conditions on the rate of competing oxidation and $H_2O_2$ decomposition is required for safe and effective scale-up. The epoxidation of sunflower (*Helianthus annuus*) seed oil using sodium tungstate catalyst and $H_2O_2$ oxidant in the absence of phase transfer agents is used as a model system. Careful analysis of the complex process and its individual steps reveals that by providing sufficient phase contact area through emulsification, the system is not mass transfer limited. However, depending on the reaction parameters, reaction progress can be strongly limited by the parallel decomposition of hydrogen peroxide. Selectivity of oxidation over decomposition, with near 100% oxidant utilization, can be achieved by balancing catalyst to acid ratios, and this would be absolutely required in large-scale industrial applications.

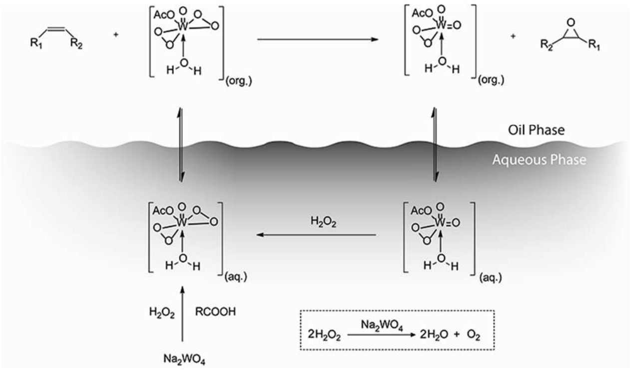

**Fig. 1** A schematic representation of the epoxidation of an alkene (sunflower seed oil in this study) with $H_2O_2$, sodium tungstate catalyst and acetic acid additive. The decomposition of $H_2O_2$ is also shown as competing reaction. (The representation of the active catalytic species follows Noyori and co-workers.[11])

## Results and discussion

In this study, stable emulsions of sunflower seed oil (SFSO) dispersed in an aqueous continuous phase are formed by homogenisation in the presence of the non-ionic surfactant Brij S10 **(**polyoxyethylene (10) stearyl ether). The aqueous phase consists of the catalyst, $Na_2WO_4$, oxidant, $H_2O_2$, and acetic acid as additive (unless otherwise specified) in common with earlier studies.[11] A non-ionic surfactant, bearing only saturated hydrocarbon chains, was selected to minimize the effect of charge at the droplet surface and to obviate competition for oxidant that would result if commonly used anionic surfactants, bearing unsaturated fatty acids, were employed. In contrast to most previous studies, no added phase transfer catalyst to facilitate the transfer of the catalytic active species between phases was used.

According to the reaction mechanism proposed in the literature for the oxidation reactions with $H_2O_2$ using tungsten-based catalysts,[11,12] the rate of the epoxidation reaction would be expected to be directly proportional to the catalyst concentration. However, initial studies, conducted at 60 °C (with constant $H_2O_2$ and $CH_3COOH$ concentrations) and varying $Na_2WO_4$ catalyst concentration between 0.01 and 0.5 *M*, yielded surprising results, Figure 2. While initially the rate of reaction increases linearly with increased catalyst concentration (Region I), this appears to plateau at $Na_2WO_4$ concentrations above ~0.04 *M* (Figure 2, region II) and then to decrease sharply at $Na_2WO_4$ concentrations above 0.25 *M* (Figure 2, region III).

In a bi-phasic system, the rate of reaction becoming apparently independent of the catalyst concentration, region II, can be interpreted as a diffusion limitation of the active oxidant species between the aqueous and the oil phases. However, variation of the oil droplet sizes in the emulsion system, and consequently variation of the specific inter-phase surface area (in accordance with BS 2955 : 1993) between 0.3 and 3 $m^2$ $g^{-1}$, does not materially affect the rate of SFSO epoxidation, suggesting that the system is not mass transfer limited under these conditions.

In many previous studies, authors have assumed that the reported lack of activity of tungstate catalysts towards $H_2O_2$ decomposition holds at all catalyst concentrations. However, a study of the rate of $H_2O_2$ decomposition over the range of the studied catalyst concentration range provides a somewhat different picture, Figure 2 secondary y-axis. While $H_2O_2$ decomposition is negligible in regions I and II, elevation of the catalyst concentration above 0.25 *M* results in a rapid increase in the rate of decomposition of $H_2O_2$ and thus an apparent sharp decrease in alkene epoxidation, as the oxidant concentration drops catastrophically. At these high catalyst concentrations, the rate of $H_2O_2$ decomposition dominates the system, almost completely suppressing the epoxidation reaction at the highest catalyst concentration due to oxidant starvation.

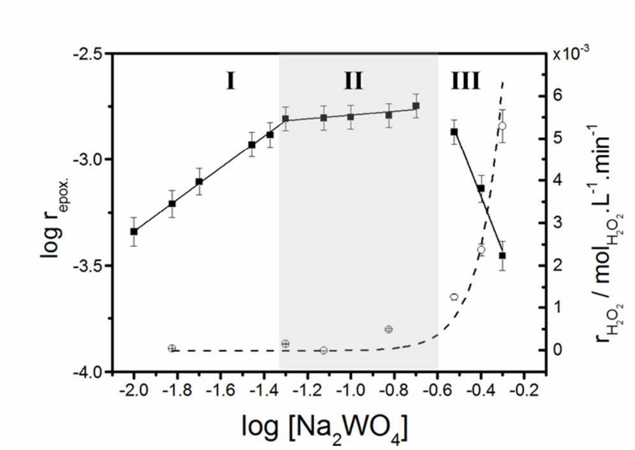

**Fig. 2** Dependence of the rate of epoxidation of SFSO (1.45 *M* unsaturation, ■, $r_{epox}$ = x $mol_{epox}$ $L^{-1}$ $min^{-1}$) and rate of $H_2O_2$ decomposition (○) on the molar concentration of the $Na_2WO_4$ catalyst. T = 60 °C, [$H_2O_2$] = 3.0 *M*, [AcOH] = 1.0 *M*.

To probe region II more carefully, a second set of reactions was conducted maintaining the molar ratio of acetic acid to $Na_2WO_4$ at 20. In Figure 2, this corresponds to the molar ratio of catalyst to acid at the inflection point between regions I and II (encircled). As before, the initial $H_2O_2$ concentration is kept constant at 3 *M*. As illustrated in Figure 3a, this provided a system in which the rate of epoxidation increased proportionally to the catalyst concentration within the studied catalyst concentration range (up to 0.5 *M*). At this constant $Na_2WO_4$:$CH_3COOH$ ratio the higher concentration of acetic acid with respect to those in Figure 2, especially noticeable at high catalyst concentrations effectively nullified the parallel decomposition of hydrogen peroxide (shown on the secondary y-axis of Figure 3).

Under these conditions, it is important to highlight the high observed rate of reaction with near 100 % oxidant utilization yield and no potentially dangerous $H_2O_2$ decomposition (which results in formation of $O_2$), making this green oxidation pathway attractive for large-scale industrial applications. One can countenance the use of relatively high catalyst concentrations as the use of bi-phasic emulsion systems could facilitate the recyclability of the catalyst by easing product separation – a process that we are currently developing elsewhere.

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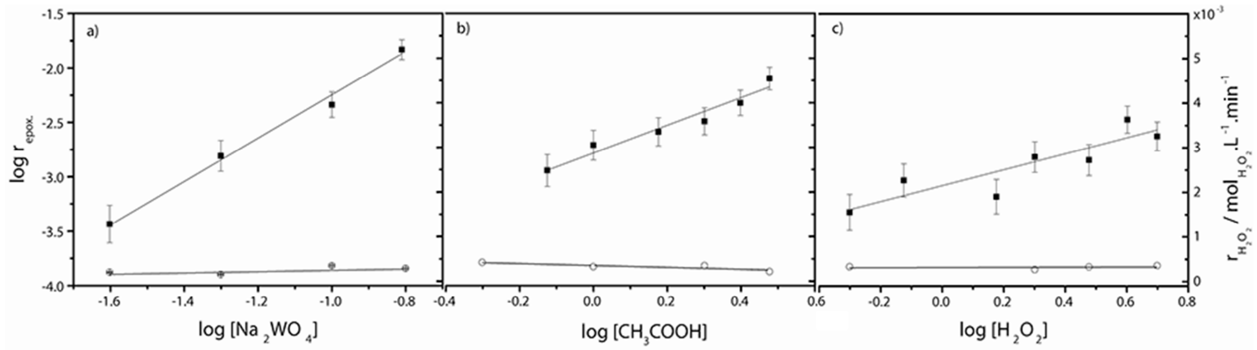

**Fig. 3** Dependence of the rate of epoxidation of SFSO (1.45 *M* unsaturation, ■, $r_{epox}$ = x $mol_{epox}$ $L^{-1}$ $min^{-1}$) and $H_2O_2$ decomposition reaction rates (○) at 60 °C on (a) sodium tungstate concentration with $[H_2O_2]$ = 3.0 *M* and $[Na_2WO_4]$:$[CH_3COOH]$ ratio = 0.05; b) acetic acid concentration with $[H_2O_2]$ = 3.0 *M*, $[Na_2WO_4]$ = 0.1 *M*; and c) hydrogen peroxide concentration with $[CH_3COOH]$ = 1.0 *M* and $[Na_2WO_4]$ = 0.1 *M*.

While decomposition of hydrogen peroxide in the presence of transition metals is well known, tungstate based catalysts are generally considered to show little peroxidase activity. Kamata *et al.*[12] show that tungstic acid ($H_2WO_4$) does not decompose hydrogen peroxide to any measurable extent, although, the $H_2O_2$ oxidation efficiency decreases dramatically in the presence of basic tungsten catalysts such as $K_2WO_4$ (showing a 32 % $H_2O_2$ yield), or basic additives (e.g. $Et_3N$). Similarly, here, extremely rapid decomposition of $H_2O_2$ is observed in the presence of $Na_2WO_4$ in the absence of acid, (which resulted in a mildly basic solution: pH 9[23]). In these cases, rapid evolution of oxygen gas causes foaming of the reaction medium due to the presence of the surfactant. The addition of acids, such as $H_3PO_4$, HCl or $HNO_3$ can successfully suppress $H_2O_2$ decomposition, dependent on their concentration.[24] This is also in agreement with the observation that in systems containing phase transfer catalysts (PTCs) bearing acidic anions, such as methyltrioctylammonium hydrogensulfate (used in Noyori's elegant work [11]). The PTC not only facilitates the transfer of the active catalytic species between phases but also plays a key role suppressing the hydrogen peroxide decomposition. Indeed, we have confirmed that even at the relatively low catalyst concentration of 3.3 mM, the hydrogen peroxide decomposition is rapid and total within 30 minutes at 60ºC in the absence of PTC. It is only upon addition of methyltrioctylammonium hydrogensulfate with a 1:1 ratio respect to tungsten, that the peroxide rate of decomposition is severely retarded to a point where it could be considered negligible. Interestingly, the use of the corresponding chloride PTC (methyltrioctylammonium chloride, Aliquat 336®) does not suppress the decomposition of hydrogen peroxide. In such systems additional mineral,[25] or organic[23] acids are required for the successful oxidation using hydrogen peroxide in bi-phasic systems.

To complete the study, the effect of acetic acid and hydrogen peroxide concentrations on the rate of epoxidation are examined, Figures 3b and 3c. Clearly the effect of increasing $[CH_3COOH]$ is significant, pointing to direct involvement of acetic acid in the bi-phasic oxidation reaction. This is usually ascribed to the organic acid binding to the catalyst W-centre[11,26] with the resultant withdrawal of electron density from the central metal acting to increase the electrophilicity of haptically bound peroxo species, although organic peracids alone can be used to effect epoxidation of alkenes.[27] Clearly, in a bi-phasic system such as this, transfer of the active oxidant species to the oil phase is a key step in the process. Whether this active oxidant species is an organic acid tungstate peroxo complex, or simply the peracid itself, is not possible to distinguish in the experiments conducted here, nor does this lack of distinction have any bearing on the scalability of the bi-phasic process.

A comparison of the rate of SFSO epoxidation in the presence of a range of organic carboxylic acids of very similar pKa, but varying lipophilicity (as defined by the octanol/water partition coefficient) was conducted. The rate of epoxidation follows a clear trend, increasing with increasing chain length up to butanoic acid, Table 1. At longer chain lengths (> $C_4$), the rate of epoxidation shows a significant decrease, which we postulate to be due to the reduced solubility of these lipophilic acids in the aqueous phase.

**Table 1** Comparison of the rate of epoxidation of SFSO in the presence of organic acids of increasing lipophilicity at 60 °C, $[H_2O_2]$ = 3.0 *M*, $[Na_2WO_4]$ = 0.1 *M* and [acid]:$[Na_2WO_4]$ = 0.05.

| **R, RCOOH** | **pKa**[a] | **log $P_{o/w}$**[a] | **solubility in $H_2O$ at 25 °C**[a] **/ g $kg^{-1}$** | **$r_{epox.}$ / mmol $L^{-1}$ $min^{-1}$** |
|---|---|---|---|---|
| $CH_3$ | 4.79 | -0.17 | miscible | 4.57 |
| $CH_3CH_2$ | 4.87 | 0.33 | miscible | 12.30 |
| $CH_3(CH_2)_2$ | 4.82 | 0.79 | miscible | 16.22 |
| $CH_3(CH_2)_3$ | 4.83 | 1.39 | 45 | 1.26 |
| $CH_3(CH_2)_4$ | 4.85 | 1.92 | 11 | 0.30 |

[a] Data from the CRC Handbook of Chemistry and Physics 94th Ed. .

Not surprisingly, the SFSO epoxidation reaction rate is also directly dependent on the concentration of hydrogen peroxide as oxidant, Figure 3c, showing a first order dependency. This observation is in agreement with the reaction mechanism where the active catalytic species is initially formed by the oxidation of $Na_2WO_4$ by two molecules of $H_2O_2$ forming $Na[WO(O_2)_2(OH)_2]$ and the posterior regeneration by one molecule of $H_2O_2$ during the catalytic cycle.[11] In a previous kinetic study by Kamata *et al.*,[26] an apparent zero order dependence on the concentration of hydrogen peroxide in the epoxidation of an internal allylic alcohol is likely to be a pseudo-zero order due to the huge excess of $H_2O_2$ used (150-350 equivalents, compared to 5-50 equivalents in this study). It is important to highlight that, at an $H_2O_2$ concentration as high as 6 *M*, decomposition can nonetheless be suppressed by keeping the $[Na_2WO_4]$: $[CH_3COOH]$ ratio below 0.05 having profound effects on the potential large-scale application of the process.

At industrial scale, catalyst and unreacted hydrogen peroxide recyclability also needs to be considered if the process is to be economically and environmentally feasible. The surfactant-stabilised system presented here has been used to study the effect of interface area by providing stable droplets allowing for tuneable surface area of phase contact. However, oil droplets dispersed in water can be formed by mechanical means, such as homogenisation, or membrane emulsification[28,29] in the absence of surfactants and such unstabilised transient emulsions provide opportunities for product isolation: separation of the catalyst and unreacted hydrogen peroxide would take place spontaneously due to the phase density difference requiring no further energy input (passive phase separators are well known in the industry). Initial experiments, using non-stabilised emulsions formed in a conventional T-junction microdevice, yielded similar initial reaction rates to those measured in this study providing confidence that the insight gained here will provide the basis for further scale-up in. Indeed, we are currently developing a larger scale continuous. Careful balance of reaction and separation rates for complete process integration would need to be achieved.

## Conclusions

Although the epoxidation of sunflower oil with hydrogen peroxide using sodium tungstate catalyst is mass transfer limited when carried out in standard bi-phasic systems, this limitation can be easily overcome by increasing the interphase area through emulsification. Under the conditions studied, an interphase surface area of 0.3 $m^2$ $g^{-1}$, or above, obtained by simple homogenisation, offers sufficient contact area to avoid physical limitations. However, a detailed study of the process under different conditions reveals potential chemical limitations: specifically, the parallel decomposition of hydrogen peroxide. We have consistently found sodium tungstate to be very active for the decomposition of hydrogen peroxide, therefore, its use mandates careful control of additives. Commonly used phase transfer catalysts can be substituted by readily available water soluble organic carboxylic acids, which not only suppress the peroxide decomposition but are also key to the reaction itself. Careful consideration of the catalyst to acid ratios allows a near 100% oxidant utilization, overcoming the safety concerns associated with the use of hydrogen peroxide as a highly efficient green alternative to toxic stoichiometric oxidants in large-scale industrial applications.

## Acknowledgments

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## Experimental

Brij S10 (av. $M_n$ = 711), sodium tungstate dihydrate (≥99.0 % purity), glacial acetic acid and hydrogen peroxide (35 wt % aqueous solution, stabilised) were purchased from Sigma-Aldrich and used without further purification. Sunflower seed oil was purchased from J. Sainsbury plc.

$^1H$ NMR spectra were recorded at 250 MHz on a Bruker Advance 250 spectrometer. Samples were dissolved in $CDCl_3$ and referenced to the residual $CHCl_3$ resonance. Droplet sizes / surface area were measured on a Malvern Mastersizer X (Malvern Instruments Ltd.) equipped with a dispersion unit.

### Emulsification

Oil in water emulsions with water:oil:surfactant mass ratio 80:18.18:1.82 were formed using a handheld homogeniser (IKA Werke; Ultra Turrax T25) at 13500 rpm for 10 minutes. The typical mixture consisted of ultra-purified water (MilliQ; Millipore Corp), sunflower seed oil and Brij S10 surfactant. The surface area averaged droplet size, D[3,2], as defined in British Standard BS 2955: 1993, was measured as an average of three repeat measurements across three repeat formulations.

### Epoxidation Reactions

A typical reaction consisted of a mixture of the pre-made emulsion described above and an aqueous solution containing the sodium tungstate catalyst, acetic acid and hydrogen peroxide (the catalyst solution). The emulsions and catalyst solution were pre-heated to the requisite reaction temperature separately before combination. The final emulsion, with a water:oil:surfactant ratio of 89:10:1 retained the droplet size of the dispersed phase formed in the absence of the catalyst solution as verified by comparison of droplet sizes determined by Mastersizer X analysis.

A range of reaction temperatures was tested and 60 ºC was selected to achieve measurable initial rates of reaction across the entire range of conditions studied. Once the reaction temperature was reached, batch epoxidation reactions were carried out in stirred glass vessels immersed in an oil bath to control the temperature. For a model reaction, the droplet size of the dispersed phase was monitored with respect to time, confirming its invariability throughout the course of the reaction (at low absolute conversion). Aliquots of reaction mixture were removed periodically and the unreacted and epoxidized oil extracted into CDCl3, separated, dried by passage through magnesium sulfate and subjected to $^1H$ NMR analysis in triplicate. The relative conversion of alkene to epoxide was followed by comparison of the integrated area of the alkene signals at 5.25-5.50 ppm with that of the triplet corresponding to the epoxide signals at 2.96 ppm, using the glycerol signals as internal standard (4.4-4.0 ppm, m). The rate of reaction is defined as the moles of double bond epoxidized per unit of time (appearance of epoxide assuming 100 % selectivity) and volume of disperse phase. The rate of reaction values were determined from the reaction profile data with conversions below 20% and the error bars in the graphs represent the standard deviation of the rate based on the error propagation of triplicate values of the conversion at each time point.

$H_2O_2$ was assayed periodically by removal of aliquots from reaction mixtures, acidification with aqueous $H_2SO_4$ (0.04 *M*) and colorimetric titration against potassium permanganate.

## Notes and references

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