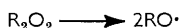


### 942. *The Properties and Reactions of Dimethanesulphonyl Peroxide.*

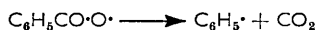
By R. N. HASZELDINE, R. B. HESLOP, and J. W. LETHBRIDGE.

Some of the properties of dimethanesulphonyl peroxide have been investigated and compared with those known for other acid peroxides. The decomposition of this peroxide in solution is almost invariably a first-order process. The energy of activation varies from 23 to 30 kcal., and the half-life at 30° from 1 to 5 hours depending on the solvent used. The rate-determining step is considered to be the homolytic fission of the peroxide bond to give methanesulphonate radicals,  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$ . These abstract hydrogen from the solvent or attack an aromatic nucleus to give methanesulphonate esters and methanesulphonic acid. Chain decomposition or carbon-sulphur bond fission is not observed. The effect of the monomers styrene and methyl methacrylate on the decomposition of the peroxide in solution is reported.

COMPARED with organic carboxylic peroxides little is known of the corresponding sulphonyl peroxides. The initial step in the decomposition of most simple organic peroxides is homolytic fission of the oxygen-oxygen bonds: <sup>1</sup>



Heterolytic fission or multiple bond rupture can occur, particularly with asymmetrical peroxides.<sup>2</sup> Amines and other strong nucleophiles can attack the peroxide oxygens and cause fast second-order decomposition.<sup>3</sup> The decomposition of carboxylic acid peroxides is complicated because the radicals decarboxylate,<sup>4</sup> e.g.,



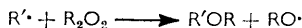
<sup>1</sup> Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; Levy, Steinberg, and Szwarc, *ibid.*, 1954, **76**, 5978; Levy and Szwarc, *ibid.*, 1954, **76**, 5981.

<sup>2</sup> Bartlett and Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 3030; Honsberg and Leffler, *J. Org. Chem.*, 1961, **26**, 733.

<sup>3</sup> Denney and Denney, *J. Amer. Chem. Soc.*, 1960, **82**, 1389; Greenbaum, Denney, and Hoffmann, *ibid.*, 1956, **78**, 2563.

<sup>4</sup> Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

and induced chain decomposition occurs:



either directly, or after interaction with the solvent.

Dimethanesulphonyl peroxide has now been prepared by electrolysis of methanesulphonic acid, and the kinetics of its decomposition in a variety of solvents has been determined. Thermal decomposition proceeds smoothly, to give methanesulphonate radicals which react directly with the solvent without chain decomposition or carbon-sulphur bond fission.

Comparison of the decomposition of this peroxide with that of the structurally similar peroxydisulphates<sup>5</sup> is difficult, for the latter are ionic, and have been studied only in aqueous media. Some comparison can be made with the less stable dibenzenesulphonyl peroxide<sup>6</sup> and with acetyl cyclohexanesulphonyl peroxide.<sup>7</sup>

The induced chain decomposition of carboxylic acid peroxides can be largely suppressed by addition to the peroxide solutions of radical scavengers such as styrene,<sup>4</sup> but with dimethanesulphonyl peroxide styrene is found to catalyse the peroxide decomposition.

## EXPERIMENTAL

*Preparation and Physical Properties of Dimethanesulphonyl Peroxide.*—The preparation of dimethanesulphonyl peroxide has been described only briefly in the patent literature.<sup>8</sup> No method of purification was given and only an active-oxygen analysis figure was reported.

In the present preparation a glass tube (50 ml. total volume), sealed at one end, in which platinum sheet electrodes (1.5 cm. square, 0.5 cm. apart) were suspended, was used as the cell, with 10M methanesulphonic acid (25 to 30 ml.) as electrolyte. The cell was cooled externally in a glycol bath at  $-10^\circ$ . A current of 0.5 ampere passed at 6 v deposited a solid coat of peroxide on the anode, raised the cell resistance, and caused the temperature to rise to  $3-5^\circ$ . If too much peroxide accumulated on the anode, and in suspension in the electrolyte, a slight explosion occurred. Electrolysis was therefore discontinued after about 2 hr. to allow the peroxide to be filtered off, and continued again after fresh acid had been added. By thus recycling, 20.0 g. of acid yielded 15.0 g. of crude peroxide (75% yield). The current efficiency was 22%. The spent electrolyte contained a small quantity of sulphate ion, indicating that some carbon-sulphur bond cleavage had occurred.

Dimethanesulphonyl peroxide, purified by washing with water then freeze-drying, is a white, amorphous solid, insoluble in water. It decomposes slowly in most common solvents, even at room temperature, and purification is difficult. Recrystallisation is achieved by dissolving the peroxide at room temperature in carbon tetrachloride containing 10% of chloroform. The peroxide which crystallises when the solution is cooled to  $-20^\circ$  is filtered off, washed with carbon tetrachloride, and dried (recovery 85%).

For elemental microanalysis, 20-mg. samples, sealed in small glass ampoules, were warmed to  $60^\circ$  to decompose the peroxide, and then opened inside the conventional analytical combustion train for the determination of carbon, hydrogen, and sulphur. Active oxygen, [O], was estimated iodometrically in the pure *dimethanesulphonyl peroxide* (Found: C, 12.5; H, 3.5; [O], 8.1; S, 33.7.  $C_2H_6O_6S_2$  requires C, 12.6; H, 3.2; [O], 8.4; S, 33.7%).

*Iodometric Estimation of Dimethanesulphonyl Peroxide.*—A reproducible, sharp end-point was obtained when aqueous sodium iodide was well shaken with the peroxide in carbon tetrachloride solution, no co-solvent being used. With solutions of the peroxide in benzene, toluene, and di-n-butyl ether, and the same technique, the end-point drifted slightly although this did not affect the precision. The active oxygen in dimethanesulphonyl peroxide was thus determined by dissolving a known weight of the peroxide in carbon tetrachloride, adding aqueous sodium iodide, and estimating the iodine liberated; the method has a systematic

<sup>5</sup> Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.

<sup>6</sup> Crovatt and McKee, *J. Org. Chem.*, 1959, **24**, 2031.

<sup>7</sup> Razuvaev, Likhterov, and Etlis, *J. Gen. Chem. (U.S.S.R.)*, 1961, **31**, 253.

<sup>8</sup> Jones and Friedrich, *U.S.P.* 2,619,507/1952.

error of about 4%. The isopropyl alcohol acetic acid<sup>9</sup> or acetic anhydride<sup>10</sup> iodometric methods for the estimation of organic peroxides were not suitable, since only slow liberation of iodine occurred, and the end-point was indistinct.

TABLE 1.

Decomposition of dimethanesulphonyl peroxide in benzene.

Temp.:	20°		Time (min.)	25°		Time (min.)	30°	
	Titre (ml.)	ln titre		Titre (ml.)	ln titre		Titre (ml.)	ln titre
0	6.18	1.82	0	5.65	1.73	0	9.52	2.25
30	5.85	1.77	30	4.99	1.59	10	8.70	2.16
60	5.36	1.68	60	4.30	1.46	20	7.98	2.08
90	5.00	1.61	90	3.76	1.32	30	7.28	1.98
120	4.65	1.54	120	3.29	1.19	40	6.69	1.90
150	4.40	1.48	150	2.80	1.03	50	6.13	1.81
180	4.05	1.40	180	2.50	0.92	60	5.63	1.73
210	3.75	1.32	210	2.16	0.77	70	5.17	1.64
240	3.52	1.26	240	1.86	0.62	80	4.73	1.55

*Thermal Stability of Solid Dimethanesulphonyl Peroxide.*—The recrystallised peroxide melted sharply at 79°; decomposition, sometimes explosive, followed immediately. During experiments to determine the decomposition products of the solid peroxide, a sample in a sealed glass tube exploded violently at 70°. Decomposition of the peroxide was negligible below 50°. At 50—60° decomposition was slow; the gaseous products included oxygen, sulphur dioxide (5% yield), ethane (15% yield), and carbon dioxide (1% yield). About 5% of the peroxide was accounted for as methanesulphonic acid, and the residual non-volatile product was an oil soluble in both water and ether.

*Decomposition of Dimethanesulphonyl Peroxide in Various Solvents.*—Reagent grade di-n-butyl ether, AnalaR benzene, sulphur-free toluene, and reagent-grade carbon tetrachloride were redistilled before use.

In each experiment 100 to 125 ml. of the solvent was added to a known weight (*ca.* 0.1 g.) of dimethanesulphonyl peroxide; the flask was shaken thoroughly and then placed in a thermostat maintained to within  $\pm 0.05^\circ$ . After temperature equilibrium was reached, 10 ml. aliquot portions were withdrawn and analysed at suitable time intervals. Initial titres varied from 2.5 to 10.0 ml. of 0.01N sodium thiosulphate solution. In each experiment about 10 readings were taken, down to about 1.0 ml. of thiosulphate; thus the reaction was followed until 50—90% of the peroxide had decomposed.

The variation of velocity constant with initial peroxide concentration was not studied in detail, but no concentration dependence was apparent over a four-fold variation in the peroxide concentration.

Results for three typical experiments at different temperatures, using benzene as solvent, are given in Table 1. Peroxide concentration is expressed as the volume of 0.01N sodium thiosulphate equivalent to a 10 ml. portion. Results are reproducible to within 5%.

The results obtained with other solvents are summarised and compared with those obtained with benzene as solvent in Table 2.

Additional experiments showed that the following caused little change in these velocity constants. (a) The exclusion of oxygen by use of solvents specially purified under a nitrogen atmosphere, and by carrying out the kinetic experiments with only nitrogen above the surface of the solutions. (Benzene, 20°,  $10^5k = 4.35 \pm 0.13 \text{ sec.}^{-1}$ ; di-n-butyl ether, 25°,  $10^5k = 6.45 \pm 0.17 \text{ sec.}^{-1}$ .) (b) The glass/liquid interface increased tenfold. (Di-n-butyl ether, 25°,  $10^5k = 6.75 \pm 0.13 \text{ sec.}^{-1}$ .) (c) The presence in solution of hydrochloric acid and benzenesulphonic acid. (Benzene, 23°, total acid 0.044N,  $10^5k = 5.74 \pm 0.08 \text{ sec.}^{-1}$ ; benzene without acid,  $10^5k = 6.10 \pm 0.08 \text{ sec.}^{-1}$ .)

*Products of Reaction of Dimethanesulphonyl Peroxide with Solvents.*—Solutions of the peroxide in benzene, in toluene, and in carbon tetrachloride were degassed, sealed in glass tubes, and left at room temperature until the peroxide had decomposed completely. The tubes were

<sup>9</sup> Wagner, Smith, and Peters, *Ind. Eng. Chem., Analyt.*, 1947, **19**, 976.

<sup>10</sup> Nozaki, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 583.

TABLE 2.

Solvent	Temp.	Velocity constant ( $\text{sec.}^{-1} \times 10^6$ )	Activation energy (kcal.)
Benzene .....	20°	3.91 ± 0.13	
„ .....	25	7.80 ± 0.23	23.1 ± 0.8
„ .....	30	14.42 ± 0.20	
Carbon tetrachloride .....	30	3.78 ± 0.03	
„ .....	35	8.92 ± 0.25	30.0 ± 1.0
„ .....	40	18.90 ± 0.05	
Di-n-butyl ether * .....	25	6.1 ± 0.3	
„ .....	30	12.4 ± 0.3	26.2 ± 1.2
„ .....	35	24.9 ± 1.2	
Toluene .....	20	20.0 ± 0.2	
„ .....	25	43.8 ± 0.2	27.4

\* Slight deviation from first-order kinetics was observed after *ca.* 60% decomposition.

cooled in liquid nitrogen before being opened into a vacuum system; no gaseous reaction product was detected.

(a) *Benzene.* The peroxide decomposed in benzene to give a yellow solution, and a heavier, dark, oily layer which was shown to be impure methanesulphonic acid by alkali titration and isolation of the sodium salt. When the excess of solvent was distilled from the yellow solution a pale yellow powder remained, which on sublimation gave colourless needles, m. p. 58°. This product was shown to be phenyl methanesulphonate (i) by prolonged aqueous alkaline hydrolysis to give phenol, (ii) by a mixed melting point with authentic material (m. p. 60°, mixed m. p. 59°), and (iii) by elemental analysis (Found: C, 48.8; H, 4.8; S, 18.4. Calc. for  $\text{C}_7\text{H}_8\text{O}_3\text{S}$ : C, 48.7; H, 4.7; S, 18.6%).

In a typical experiment, 0.5 g. of peroxide was dissolved in 10.0 g. of benzene; after reaction, 60% of the peroxide was accounted for as methanesulphonic acid, and 30% as phenyl methanesulphonate. No indication was found of di- or tri-substituted products, and the 10% of material not accounted for was not present as sulphur dioxide or sulphate. From the weight of benzene recovered one mole of peroxide reacts with approximately one mole of benzene. No evidence was found for any products arising from the fission of the carbon-sulphur bond.

(b) *Toluene.* The decomposition of dimethanesulphonyl peroxide in toluene also gave a pale yellow oil together with a dark, oily, water-soluble layer, which was almost entirely methanesulphonic acid. Distillation of the yellow oil at 125°/4 mm. left a residue consisting mainly of *p*-tolyl methanesulphonate, purified by molecular distillation at 50°. The material volatile at 125°/4 mm. was fractionally crystallised from ethanol at low temperature to give fractions containing respectively *p*-, *o*- and *p*-, and *o*- and *m*-tolyl methanesulphonates. Elemental analysis and hydrolysis, combined with infrared spectroscopic analysis, characterised the esters. Bands at 12.1 and 14.7  $\mu$  distinguished the *para*- from the *meta*- and *ortho*-isomers, respectively; bands at 10.3 and 13.85  $\mu$  were characteristic for the *ortho*-ester, and a band at 10.7  $\mu$  was unique for the *meta*-ester.

Authentic specimens of the esters were prepared from the sodium cresates and methanesulphonyl chloride and recrystallised from ethanol at -78°. Only the *para*-isomer has been reported previously:<sup>11</sup> *para*-isomer (Found: C, 51.8; H, 5.4; S, 17.2) m. p. 42°; *ortho*-isomer (Found: C, 51.1; H, 5.5; S, 17.2) m. p. -5°; *m*-isomer (Found: C, 52.1; H, 5.6; S, 17.0) m. p. 25°.  $\text{C}_8\text{H}_{10}\text{O}_3\text{S}$  requires C, 51.6; H, 5.6; S, 17.2%). In a typical experiment 5.0 g. of peroxide was dissolved in 500 g. of toluene; after reaction 55% of the peroxide was accounted for as methanesulphonic acid, and 34% as tolyl methanesulphonates (*o*-34; *m*-6; *p*-60% approx.). From the weight of toluene recovered it was seen that one mole of peroxide reacts with approximately one mole of toluene. No product was found arising from the fission of the carbon-sulphur bond. Bands characteristic of dibenzyl or benzyl methanesulphonate were absent from the infrared spectra of the organic products. An unidentified residue accounted for approximately 2% of the total product.

(c) *Carbon tetrachloride.* The peroxide (0.525 g.) was sealed with degassed carbon tetrachloride (9.75 g.) and kept at 35° for 36 hr. No product more volatile than the solvent was then present. The excess of solvent was removed *in vacuo* and the remaining dark, complex mixture was shaken with cold water (5 $\times$ ) to give an aqueous solution containing methanesulphonic acid

<sup>11</sup> Looker and Thatcher, *J. Org. Chem.*, 1954, **19**, 784.

equivalent to 64% of the original peroxide. The aqueous extract contained very little free chloride ion and no sulphate. The water-insoluble residue was soluble in acetone and was not investigated further.

*Decomposition of Dimethanesulphonyl Peroxide in Solutions containing Monomers.*—Uninhibited styrene was redistilled. Reagent methyl methacrylate was freed from inhibitor by shaking it with aqueous sodium hydroxide, dried ( $\text{Na}_2\text{SO}_4$ ) and redistilled under nitrogen at reduced pressure. AnalaR benzene was redistilled.

A series of preliminary experiments was carried out to establish that polymerisation of styrene or methyl methacrylate occurred only when the peroxide was present. To a solution of the monomer in benzene (1:1 by volume), prepared in a nitrogen atmosphere, was added approximately 1% by weight of the peroxide. The solution was shaken at room temperature for 5–12 hr. then poured into an excess of methanol to precipitate the polymer (5–60% yield), which was washed, dried and weighed. Methyl methacrylate polymerised more readily than styrene. Blank experiments gave no polymer.

(a) *Styrene.* Styrene markedly increased the rate of peroxide decomposition, so much so that reaction was immediate and the decomposition could not be followed kinetically with molar solutions of styrene in benzene, carbon tetrachloride, or di-n-butyl ether. Kinetic data obtained for styrene concentrations near to 0.01N in benzene or in di-n-butyl ether are shown in Table 3.

TABLE 3.

Effect of styrene on the decomposition of dimethanesulphonyl peroxide in solution.

Solvent	Styrene[S] (mole/l.)	Temp.	Velocity constant ( $\text{sec.}^{-1} \times 10^5$ )	Activation energy (kcal.)
Benzene .....	0	20°	3.91	
" .....	0	25	7.80	23
" .....	0.01	20	11.5	
" .....	0.01	25	17.0	13
Di-n-butyl ether .....	0	25	6.17	
" .....	0	35	24.9	26
" .....	0.01	20	7.25	
" .....	0.01	25	11.5	16
" .....	0.002	25	8.0	
" .....	0.024	25	20.5	—

In both benzene and di-n-butyl ether the decomposition of dimethanesulphonyl peroxide is still of first order. The velocity constant for the decomposition of the peroxide in solutions containing styrene is given by the expression:

$$k = A + B[S] \text{ sec.}^{-1},$$

where  $A$  and  $B$  are constants. For di-n-butyl ether at 25°  $A$  is  $6.17 \times 10^{-5}$  and  $B$  is  $5.9 \times 10^{-3}$ .

(b) *Methyl methacrylate.* High concentrations of methyl methacrylate in benzene, toluene or di-n-butyl ether reduced the rate of peroxide decomposition in these solvents, and the effect was proportional to the monomer concentration. The high concentration of monomer interferes with the observation of the end-point in di-n-butyl ether, making kinetic work difficult and unreliable. The kinetic results for solutions in benzene and toluene are summarised in Table 4.

TABLE 4.

Effect of methyl methacrylate on the decomposition of dimethanesulphonyl peroxide in solution.

Solvent	Methyl methacrylate [MMA] (mole/l.)	Temp.	Velocity constant ( $\text{sec.}^{-1} \times 10^3$ )	Activation energy (kcal.)
Benzene .....	1.0	20°	3.05	
" .....	1.0	25	5.80	22.5
Toluene .....	0	25	43.8	
" .....	1.0	25	36.2	—
" .....	2.0	25	30.8	

The velocity constant for the decomposition of dimethanesulphonyl peroxide in solutions containing methyl methacrylate is given by the expression:

$$k = C - D[\text{MMA}] \text{ sec.}^{-1}.$$

For solutions in toluene at 25°,  $C$  is  $43.8 \times 10^{-4}$  and  $D$  is  $6.5 \times 10^{-5}$ .

4906 *The Properties and Reactions of Dimethanesulphonyl Peroxide.*

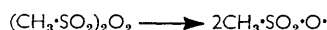
## DISCUSSION

The most characteristic feature of the decomposition of dimethanesulphonyl peroxide in solution is the close adherence to first-order kinetics in each of the solvents investigated. The relatively small variations in the values of the velocity constants for decomposition in the four solvents, benzene, toluene, carbon tetrachloride, and di-n-butyl ether, is also unusual (Table 2), although similar values have been obtained for the decomposition of acetyl cyclohexanesulphonyl peroxide in benzene and carbon tetrachloride.<sup>7</sup>

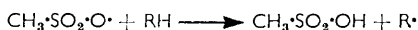
Although dimethanesulphonyl peroxide decomposes in solution about a thousand times faster than benzoyl or acetyl peroxide under similar conditions, the reaction does not involve a chain decomposition of the type observed for carboxylic acid peroxides. Such a chain decomposition (i) is usually greatly influenced by the solvent,<sup>12</sup> (ii) involves several different chain-propagating and terminating steps, and an overall order usually greater than unity,<sup>4</sup> and (iii) is generally retarded by the addition of monomers to the solution.

The change in first-order rate constant with solvent is small, but about the same as that for the decomposition of other peroxides in similar solvents where the solvent does not contribute directly to the decomposition mechanism, or where its participation in the decomposition is suppressed by the addition of a radical scavenger. A possible exception to this is the decomposition of dimethanesulphonyl peroxide in toluene, which is faster, compared with that in benzene, than might be expected from results with acetyl or benzoyl peroxides. However, the kinetics of the reaction, the products found, and the effect of monomer addition, all point to a decomposition mechanism for the peroxide in toluene similar to that in benzene, with the solvents exerting only a secondary effect.

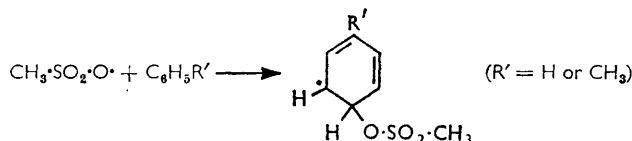
The kinetics and activation energy of the dimethanesulphonyl peroxide decomposition in benzene, toluene, di-n-butyl ether, and carbon tetrachloride suggest that the peroxide decomposes by simple homolytic fission of the oxygen-oxygen bond:



The  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$  radicals then react with hydrogen-containing solvents (a) by abstraction of hydrogen:



(b) by addition to the aromatic ring:



followed by hydrogen abstraction by a second  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$  radical to form the aryl ester and methanesulphonic acid.

The decomposition mechanism for acetyl cyclohexanesulphonyl peroxide was considered to involve homolytic bond fission or a concerted molecular process.<sup>7,13</sup> The rearrangement occurring during decomposition of methane- and ethane-sulphonylbenzoyl peroxides was later explained via acid-catalysed heterolytic fission of the peroxide bond.<sup>14</sup> The asymmetrical structure of these peroxides and the greater complexity of the radical fragments formed in their decompositions make direct comparison with the present work difficult.

Since 90% of the  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$  groups present in the original peroxide are found in the products, decomposition of the  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$  radical involving carbon-sulphur bond fission is unimportant when a substrate is present which the  $\text{CH}_3\cdot\text{SO}_2\cdot\text{O}\cdot$  radical can attack.

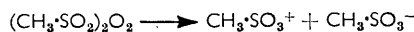
<sup>12</sup> Cass, *J. Amer. Chem. Soc.*, 1946, **68**, 1976.

<sup>13</sup> Razuvaev, Terman, Likhterov, and Etlis, *J. Polymer Sci.*, 1961, **52**, 123.

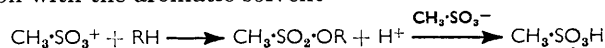
<sup>14</sup> Razuvaev, Likhterov, and Etlis, *Tetrahedron Letters*, 1961, 527.



Heterolytic fission of the O-O bond in dimethanesulphonyl peroxide:



followed by reaction with the aromatic solvent



would also account for the observed products. Although (i) the peroxide decomposition is not acid-catalysed, (ii) the ratio of the polymerisation rates for styrene and methyl methacrylate agrees with radical initiation rather than ionic initiation, and (iii) dibenzene-sulphonyl peroxide appears to initiate polymerisation by radical formation,<sup>6</sup> the possibility that dimethanesulphonyl peroxide decomposes by a mixed homolytic/heterolytic mechanism is not ruled out by the present work.

In the decomposition of an organic peroxide, addition of a monomer usually has two effects: (a) the peroxide acts as a radical polymerisation initiator, (b) the monomer acts as a radical scavenger. The results obtained during the present work show that dimethanesulphonyl peroxide is a polymerisation initiator.<sup>8</sup>

The marked influence of styrene on the decomposition of the peroxide is very similar kinetically to the influence of hydrogen ions in the acid-catalysed decomposition of the peroxodisulphates;<sup>5</sup> the large reduction in activation energy (10 kcal.) indicates that the styrene is here acting catalytically.

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