494. *Tracer Studies in Ester Hydrolysis. Part X.* The Hydrolysis of Methyl Toluene-*p*-sulphinate.*

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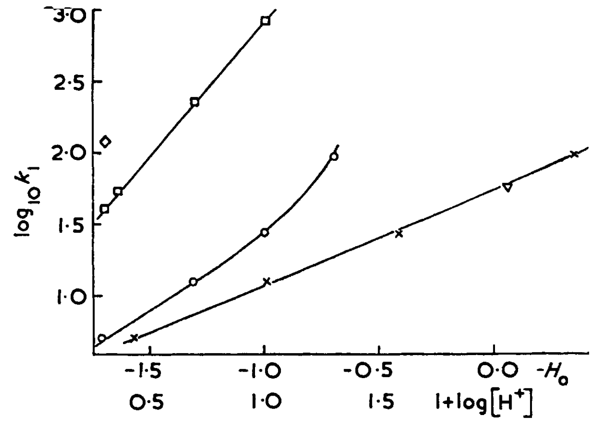
The hydrolysis of methyl toluene-*p*-sulphinate is very slow in neutral aqueous dioxan, but is acid-catalysed, and is very rapid in alkaline solution. The sulphur–oxygen bond is broken during acid or alkaline hydrolysis. Halogen acids catalyse hydrolysis by converting the ester into the readily hydrolysable sulphinyl chloride. The kinetic effects of changes of solvent, temperature, and acid concentration have been examined and interpreted.

Sulphinic acids are comparatively weak,[1] p$K_a \approx 2$, and one might expect the hydrolyses of their esters to be unlike those of alkyl sulphonates, but similar to those of organic sulphites and of carboxylic esters. Thus the isolation of an alcohol of retained configuration from the hydrolysis of (—)-1-phenylethyl *dl*-toluene-*p*-sulphinate † is evidence for sulphur–oxygen fission.[2] However, alkyl–oxygen fission must occur during the rearrangement of alkyl sulphinates to sulphones, and there is evidence for carbonium-ion intermediates in this rearrangement of diarylmethyl sulphinates in acetic acid.[3]

We have measured the rates of hydrolysis of a methyl ester in aqueous dioxan and determined the position of bond fission by the use of oxygen-18. A preliminary account has been given.[4]

Results

Because methyl-toluene *p*-sulphinate is only slightly soluble in water, aqueous dioxan was used as solvent. The rate constants are given in Table 1. For neutral and alkaline solutions the values are approximate, because neutral hydrolysis is slow and autocatalysed by toluene-*p*-sulphinic acid and the rapid reaction with hydroxide ion is only just within the range accessible to rate measurement by conventional methods. The agreement between duplicate experiments is reasonable, except at the higher concentrations of strong acid where the estimation of the liberated sulphinic acid is inaccurate.



Variation of $\log k_1$ with $\log [H^+]$ and $-H_0$.

$\log k_1$ plotted against

- ◇ log [HBr],
- □ log HCl,
- ○ log [$HClO_4$],
- × $-H_0$ for $HClO_4$,
- ▽ $-H_0$ for $HClO_4$ + $NaClO_4$.

The first-order rate constant of acid hydrolysis, k_1, is not proportional either to the concentration of acid, or to Hammett's acidity function, h_0, *e.g.*, a plot of $\log k_1$ against log [$HClO_4$] has a unit slope only at low acidities, and the corresponding plot against $-H_0$ is a straight line

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* Part IX, *J.*, 1961, 943.

† *dl* refers to the stereochemistry at the sulphur atom.

[1] Burkhard, Sellers, DeCou, and Lambert, *J. Org. Chem.*, 1959, **24**, 767.

[2] Balfe, Kenyon, and Tarnoky, *J.*, 1943, 446.

[3] Wragg, McFadyen, and Stevens, *J.*, 1958, 3603; and references cited therein.

[4] Bunton and Hendy, *Chem. and Ind.*, 1960, 446.

of slope *ca.* 0·7 (see Figure). For $[HClO_4]$ = 0·2M, a change of solvent from dioxan–water 40 : 60 (v/v) to 75 : 25 (v/v) decreases the rate; further change in the same direction increases it; the protonating power of the medium, as measured by $-H_0$, varies similarly (Tables 2 and 3).

Added salts increase the rate of acid hydrolysis, sodium chloride being much more effective than sodium perchlorate. Similarly hydrogen chloride and hydrogen bromide are much better catalysts than is perchloric acid.

The sulphur–oxygen bond is broken during both acid and alkaline hydrolysis (Table 4),

TABLE 1.

First-order rate constants, k_1, for hydrolysis of methyl toluene-*p*-sulphinate. Dioxan–water 40 : 60 (v/v) and 25·2° unless specified.

(A) *Acid.*

(i)

$[HClO_4]$ (M)	0·200	0·500	1·00	2·00
10^6k_1 (sec.$^{-1}$)	4·93, 4·98, 8·47 *	12·4	28·5	79, 85, 105

(ii) Variation of solvent: $[HClO_4]$ = 0·2M.

Dioxan–water (x : 100 − x; v/v)	40	60	65	70	75	80	90
10^6k_1 (sec.$^{-1}$)	4·96	3·37	3·15	2·50	2·36	2·48	3·14

(iii) Variation of temperature: $[HClO_4]$ = 0·2M.

Temp.	25·2°	34·9°	44·6°	60·0°
10^6k_1 (sec.$^{-1}$)	4·96	14·7	43·7	176

(iv) Effect of added salts: [NaCl] = 0·2M, unless specified.

$[HClO_4]$ (M)	0·200	0·500	1·00	2·00
10^6k_1 (sec.$^{-1}$)	33·9	100, 218 †	269, 273; 54·6,‡ 65·3 ‡	~1100

(v) Halogen acids: Hydrochloric acid unless specified.

[HX] (M)	0·100	0·200	0·228	0·500	1·00
10^6k_1 (sec.$^{-1}$)	47·5 §	41·5, 123 §	53·9	230	864

(B) *Initially neutral solution.* Initial value of k_1.

[Salt]	—	$NaClO_4$ = M/2	NaCl = M/2
10^6k_1 (sec.$^{-1}$)	0·02	≈0·003	0·23

(C) *Alkaline solution.* At 0° with [NaOH] = 2·03 × 10^{-2}M; k_2 ≈4 l. mole^{-1} sec.$^{-1}$.

* D_2O–dioxan. † NaCl = M/2. ‡ $NaClO_4$ = 1M. § HBr.

TABLE 2.

Variation of H_0 with solvent composition.

Perchloric acid unless specified.

Dioxan–water (x : 100 − x; v/v)		40 *	60	70	80	85	90
$[H_2O]$ (moles %)		87·6	75·9	66·9	54·8	46·6	34·6
H_0	$[HClO_4]$ = 0·2M	1·61	1·95, 1·87 †	2·10	2·05	2·01	1·67
	,, 0·56M	—	1·35, 1·48 †	—	—	—	—
	,, 1M	0·33	0·79	0·81	0·90	0·29	*ca.* 0·05

* Ref. 6*b*. † HCl.

TABLE 3.

Variation of hydrolysis rate and H_0 with solvent composition. $[HClO_4]$ = 0·2M at 25·2°.

Dioxan–water (x : 100 − x; v/v)	40	60	65	70	75	80	90
6 + log k_1	0·69	0·53	0·50	0·40	0·37	0·39	0·50
H_0	1·61	1·95	2·00	2·10	2·08	2·05	1·67
6 + log k_1 + H_0	2·30	2·48	2·50	2·50	2·47	2·44	2·17

TABLE 4.

Bond fission.

Dioxan–$H_2{}^{18}O$ 40 : 60 (v/v) at 25°. Isotopic abundances are in atom % excess above normal.

Reagent		$HClO_4$		NaOH	
Isotopic abundance	H_2O	0·72	0·98	0·72	0·98
	MeOH	0·00$_2$	−0·00$_5$	0·00	−0·00$_2$

and methyl chloride is not formed from added chloride ion. In none of our experiments was there any evidence for rearrangement to methyl *p*-tolyl sulphone, in accord with the evidence for carbonium-ion intermediates in this rearrangement.[3]

The values of Hammett's acidity function, H_0,[5] were determined by indicator measurements with *m*- and *p*-nitroaniline, and by using their pK values in water.[5b] Where comparisons were possible, our values agree with earlier ones[6] (Table 2). In dioxan–water 60 : 40 (v/v) the acidity functions for both hydrochloric and perchloric acid are similar at M/5; at higher concentrations hydrochloric acid has less protonating power, probably because it is then no longer fully ionised. Minima in plots of $-H_0$ against dioxan–water composition are observed for both 0·2M- and M-acid. These minima arise because addition of the organic solvent to water " salts-in " the indicator and so decreases the acidity, but further addition of the solvent converts the hydronium ion into a stronger acid, the conjugate acid of the organic solvent.[5a, 7]

DISCUSSION

Alkaline Hydrolysis.—The rapid second-order reaction between the ester and hydroxide ion is a bimolecular nucleophilic attack upon the sulphur atom:

$$\mathrm{Me{\cdot}C_6H_4{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OMe} + {}^{18}\mathrm{OH}^- \longrightarrow \mathrm{Me{\cdot}C_6H_4{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}{}^{18}O^-} + \mathrm{MeOH}$$

This mechanism is analogous to the mechanism $B_{\mathrm{Ac}}2$ observed typically in the alkaline hydrolysis of carboxylic esters and to that of the alkaline hydrolysis of dialkyl sulphites. This latter reaction is, however, the faster.[8] We do not know whether the reaction involves formation of an unstable intermediate by addition of hydroxide ion to the sulphur atom—there is no evidence for such an intermediate in the hydrolysis of sulphite esters. Alcoholysis of optically active sulphinic esters gives at least partial inversion of configuration at the sulphur atom;[9] the stereochemistry of hydroxide attack is experimentally unobservable but is probably similar to that of alcoholysis.

Neutral Hydrolysis.—Neutral hydrolysis is very slow, but is catalysed by sodium chloride, which generates the reactive sulphinyl chloride:

$$\mathrm{Me{\cdot}C_6H_4{\cdot}SO_2Me} + \mathrm{Cl^-} \longrightarrow \mathrm{MeO^-} + \mathrm{Me{\cdot}C_6H_4{\cdot}SOCl} \xrightarrow{\text{Fast}} \mathrm{Me{\cdot}C_6H_4{\cdot}SO_2H} + \mathrm{H^+} + \mathrm{Cl^-}$$

Acid Hydrolysis.—The usual tests of molecularity of acid-catalysed reactions are neither rigorous nor general. As for the acid hydrolysis of dialkyl sulphites, the hydrolysis of methyl toluene-*p*-sulphinate follows neither of the limiting kinetic forms associated with the Zucker-Hammett hypothesis.[10] As in many acid hydrolyses, k_1 increases less rapidly than required for a linear variation with h_0, but more rapidly than required for a linear variation with [H$^+$] In most of these hydrolyses, independent evidence suggests that the reaction has the bimolecular A-2 mechanism, and that the Zucker–Hammett hypothesis is then of limited validity.

The value of the entropy of activation, ΔS^*, can assist in an assignment of molecularity. It is positive, or close to zero, for many hydrolyses with the A-1 mechanism, and negative for those with A-2 mechanism.[11] There is, however, a considerable spread of values for various reactions by either mechanism, apparently depending upon the solvent and structure of the substrate.[12] The entropy of activation $\Delta S^* = -12$ e.u., is in the range

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[5] (*a*) Paul and Long, *Chem. Rev.*, 1957, **57**, 1; (*b*) Bascombe and Bell, *J.*, 1959, 1096.

[6] (*a*) Braude and Stern, *J.*, 1948, 1976, 1982; (*b*) Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

[7] Gutbezahl and Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559, 565.

[8] Bunton, de la Mare, Lennard, Llewellyn, Pearson, Pritchard, and Tillett, *J.*, 1958, 4761.

[9] Phillips, *J.*, 1925, **127**, 2569; Herbrandson and Cusano, *J. Amer. Chem. Soc.*, 1961, **83**, 2124.

[10] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[11] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2632.

[12] Whalley, *Trans. Faraday Soc.*, 1959, **55**, 798; Koskikallio and Whalley, *ibid.*, p. 815.

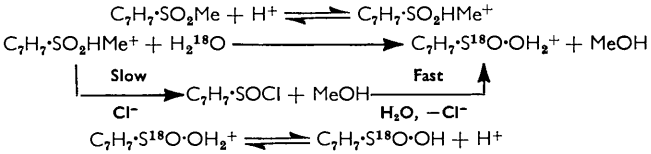
often observed for *A*-2 reactions, and moreover is similar to the values observed in bimolecular acid hydrolyses of the structurally similar dialkyl sulphites.[13] For the acid hydrolysis of dimethyl sulphite ΔS^* is *ca.* −8 e.u., but is considerably more negative (by *ca.* 10 e.u.) for the analogous hydrolysis of ethylene sulphite. This difference may be related to the differences between reactions in which a group is expelled by a reagent, and those in which attack of the reagent opens a ring. For the acid hydrolysis of diethyl sulphite in aqueous dioxan ΔS^* is appreciably more negative (by *ca.* 13 e.u.) than in water.

The deuterium solvent isotope effect, $k_{D_2O}/k_{H_2O} = 1{\cdot}7$, is characteristic of specific hydrogen-ion catalysis. For *A*-1 reactions, k_{D_2O}/k_{H_2O} is usually greater than 2, and *ca.* 1·5 or less for *A*-2 reactions,[14] but it depends so much upon the structures of the substrate and transition state that it is of limited diagnostic value.[15] To the extent that it is applicable, this test would support an *A*-2 mechanism for acid hydrolysis.

Addition of salts gives considerable mechanistic information. Their catalytic effectiveness depends upon their ability to convert the ester into a more reactive intermediate. Perchlorate ions do not do this, and addition of M-sodium perchlorate merely doubles the reaction rate. Salts may change the protonating power of the medium, and the relative activity coefficients of the initial and the transition states.[5a, 16] In our experiments, the enhancement of rate of hydrolysis by sodium perchlorate is very similar to the effect upon the acidity function (Figure). Similar observations have been made on the hydrolysis of acetic anhydride in aqueous dioxan by the *A*-2 mechanism.[17]

Halide ions are very effective catalysts, *e.g.*, addition of 0·5M-sodium chloride to 0·5M-perchloric acid increases the rate of hydrolysis twenty-fold (Table 1). This powerful catalysis is effective over the whole acidity range. The dialkyl sulphites behave similarly.[13] The role of the halide ions is to provide a new acid-catalysed reaction path by converting the ester into the reactive sulphinyl chloride. Hydrogen chloride is a very effective catalyst, comparable in efficiency with an equivalent mixture of perchloric acid and sodium chloride (Table 1). Hydrogen bromide is still more effective, in agreement with the greater nucleophilicity of bromide than of chloride ion in hydroxylic solvents. The greater acid strength of hydrogen bromide may be a contributory factor.

On the assumption that the proton is added in a rapid and reversible first step, the acid hydrolysis can be written as:



$$C_7H_7{\cdot}SO_2Me + H^+ \rightleftharpoons C_7H_7{\cdot}SO_2HMe^+$$

$$C_7H_7{\cdot}SO_2HMe^+ + H_2{}^{18}O \longrightarrow C_7H_7{\cdot}S^{18}O{\cdot}OH_2{}^+ + MeOH$$

$$C_7H_7{\cdot}SO_2HMe^+ \xrightarrow[Cl^-]{Slow} C_7H_7{\cdot}SOCl + MeOH \xrightarrow[H_2O,\ -Cl^-]{Fast} C_7H_7{\cdot}S^{18}O{\cdot}OH_2{}^+$$

$$C_7H_7{\cdot}S^{18}O{\cdot}OH_2{}^+ \rightleftharpoons C_7H_7{\cdot}S^{18}O{\cdot}OH + H^+$$

The hydrolysis of toluene-*p*-sulphinyl chloride in initially neutral aqueous dioxan is too fast to be measured by dilatometry, and is therefore considerably faster than the ester hydrolysis, even with halogen acids.

The Zucker–Hammett hypothesis is usually applied by studying the variation of rate with acid concentration in a given solvent, but alternatively one can keep the acid concentration constant and vary the solvent.[6a, 18] With methyl toluene-*p*-sulphinate there is a correlation between $\log k_1$ and $-H_0$ (Table 3); *e.g.*, both show minima for dioxan–water 75 : 25 (v/v). Such correlations have sometimes been used to assign reactions to the *A*-1 category, but our observations suggest that they may be misleading.

We conclude that the acid hydrolysis of methyl toluene-*p*-sulphinate in aqueous dioxan

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[13] Bunton, de la Mare, and Tillett, *J.*, 1959, 1766; Tillett, *J.*, 1960, 5138.
[14] Pritchard and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4162.
[15] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3207.
[16] Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3243.
[17] Bunton and Perry, *J.*, 1960, 3070.
[18] Hawke and Stimson, *J.*, 1956, 4676; and references cited therein.

is a bimolecular *A*-2 reaction. A unimolecular *A*-1 reaction involving sulphinyl cations might be important in strong acid, and such intermediates have been postulated.[19] We attempted to find evidence for them by dissolving the acid in concentrated sulphuric acid and pouring the mixture into methanol (this is a good method for the esterification of carboxylic acids which can generate acylium ions [20]). We isolated methyl toluene-*p*-sulphinate in low yield, but apart from its simplicity this method is inferior to the conventional one for the preparation of sulphinic esters.

By analogy with carboxyl reactions we write the reaction as involving sulphinyl cations:

$$C_7H_7{\cdot}SO_2H + 2H_2SO_4 \rightleftharpoons C_7H_7{\cdot}SO^+ + H_3O^+ + 2HSO_4^-$$

$$C_7H_7{\cdot}SO^+ + MeOH \longrightarrow C_7H_7{\cdot}SO_2Me + H^+$$

EXPERIMENTAL

Materials.—The solvent was made up, by weight, with water and purified dioxan [21] to correspond to the appropriate volume composition at 20° (values such as 60 : 40 v/v denote a mixture of 60 vols. with 40 vols.).

Toluene-*p*-sulphinyl chloride was prepared from the dried acid and thionyl chloride and then converted into the ester by treatment with methanol in pyridine.[3] Because of the sensitivity of sulphinic esters to halogen acids we used perchloric instead of hydrochloric acid for removal of pyridine. The ester was purified by distillation at ~70° (bath-temp.)/~10^{-2} mm. (Found: C, 55·9; H, 5·9; S, 18·6%; equiv., 173. Calc. for $C_8H_{10}O_2S$: C, 56·4; H, 5·9; S, 18·8%; equiv., 170).

The salts were commercial samples dried at 120°. Sodium perchlorate was chloride free, and prepared by neutralising perchloric acid.

Reaction in Sulphuric Acid.—Dried toluene-*p*-sulphinic acid (9 g.) was added slowly to concentrated sulphuric acid (30 c.c.) kept just above its m. p. The solution became reddish-brown, and was then kept at 0°. The whole was poured rapidly into "AnalaR" methanol (120 c.c.) at *ca.* −5°. The colour disappeared and the solution was immediately extracted with pentane. (This extraction was probably very inefficient because the residual methanol still had a smell of the ester.) The pentane layer was washed with dilute sodium hydrogen carbonate and with water (twice), dried (Na_2SO_4), and evaporated, and the residue was distilled at 10^{-2} mm. (yield 10%) (Found: C, 56·0; H, 5·9; S, 18·8%; equiv., 175). The infrared spectrum was very similar to that of the authentic methyl ester, having no absorption characteristic of either hydroxy-compounds or sulphones.

Kinetics.—Stoppered flasks were used at low temperatures, sealed tubes above 45°. The liberated acid was titrated under nitrogen with 0·01N-sodium hydroxide to phenolphthalein. For some of the acid runs the bulk of the acid was neutralised by prior addition of a standard amount of a more concentrated alkali. An example of such a run is as follows.

Dioxan–water 40 : 60 (v/v); 25·2°; [Ester] = 0·0431M; [$HClO_4$] = 0·500M; [NaCl] = 0·500M. Aliquot parts (5 c.c.) were removed and partially neutralised with 20·86 c.c. of 0·1185N-sodium hydroxide. The residual acid was titrated with 0·01N-sodium hydroxide. Details are tabulated. The infinity samples were kept in sealed tubes to eliminate any effect due to aerial oxidation.

Time (min.)	4·5	9	17	22·5	30	37	43·5	50·5	58·5
Titre (c.c.)	4·45	5·4	7·7	8·2	9·8	11·1	12·5	13·05	14·15
log (*a* − *x*) (obs.)	1·302	1·281	1·225	1·212	1·167	1·127	1·079	1·059	1·015
Calc. from k_1	1·307	1·280	1·236	1·206	1·163	1·123	1·088	1·044	1·010
Time (min.)	63	69	80	85·5	97	∞			
Titre (c.c.)	15·15	15·85	16·5	17·2	18·65	24·35	24·6	24·65	25·0 *
log (*a* − *x*) (obs.)	0·971	0·937	0·903	0·863	0·767	—	—	—	—
Calc. from k_1	0·978	0·942	0·882	0·855	0·786	—	—	—	—

10^6k_1 = 217 sec.$^{-1}$ (calc. graphically).

* Calc. from weight of ester.

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[19] Kurzer and Powell, *J.*, 1952, 3728; Allen and Reich, *J. Phys. Chem.*, 1960, **64**, 1928.

[20] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 771; Newman, "Steric Effects in Organic Chemistry," John Wiley, New York, 1956, p. 217.

[21] Vogel, "Practical Organic Chemistry," Longmans, Green, London, 1948, p. 175.

The rate of the alkaline hydrolysis is such that we were able to follow only the end of the reaction; the quoted value of the second-order rate constant k_2 is therefore approximate.

Dioxan–water 40 : 60 (v/v); $[C_7H_7{\cdot}SO_2Me] = [OH^-] = 2{\cdot}03 \times 10^{-2}$M; at 0°. Aliquot parts (5 c.c.) were added to 5 c.c. of 0·0220N-hydrochloric acid, and the acid was back-titrated with 0·01N-sodium hydroxide. Details are tabulated.

Time (min.)	0·50	0·92	1·33	2·83	7·00	∞
Titre (c.c.)	8·35	8·35	8·70	9·20	9·70	10·02
$10^{-2}/[OH^-]$ (mole^{-1})	3·03	3·03	4·00	6·25	16·6	

$k_2 \approx 4$ l. mole^{-1} sec.$^{-1}$.

Bond Fission.—The ester was hydrolysed in dioxan–$H_2{}^{18}O$. After complete reaction, methanol was distilled off, fractionated in a low-hold-up spiral-packed column (250 × 6 mm.), and purified by gas–liquid chromatography through a Celite–silicone oil column.

The isotopic abundance of the methanol was determined by converting it into carbon monoxide *in vacuo* in a red-hot carbon tube in an induction furnace. The gas was analysed mass-spectrometrically.

Because it seemed possible that halide ions catalysed the reaction by attacking the methyl group, an experiment was done with 0·2M-ester and 0·2M-hydrochloric acid at 25·2° in a stream of dry nitrogen. No chloride was lost, and therefore no methyl chloride could have been formed; loss of chloride equivalent to $<1\%$ of total reaction would have been detected.

Indicator Measurements.—Existing procedures were followed, with *m*- and *p*-nitroaniline as indicators.[5b] Unless freshly purified dioxan was used a colour developed in the drier solvents containing M-perchloric acid. This colour interfered with the measurements, and we assume it to have resulted from interaction between the amine and aldehyde or acetals (which are formed slowly in dioxan).

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