

Correlation of the Rates of Solvolysis of Electron-Rich Benzoyl Chloride Using the Extended Grunwald-Winstein Equation

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The solvolysis rate constants of piperonyloyl chloride (**1**) in 27 different solvents are well correlated with the extended Grunwald-Winstein equation, using the N_T solvent nucleophilicity scale, Y_{Cl} solvent ionizing scale, and I aromatic ring parameter with sensitivity values of 0.30 ± 0.05 , 0.71 ± 0.02 , and 0.60 ± 0.04 for l , m , and h , respectively. The solvent kinetic isotope effect values (SKIE, k_{MeOH}/k_{MeOD} and $k_{50\%MeOD-50\%D_2O}$) of 1.16 and 1.12 were also in accord with the values for the S_N1 mechanism and/or the dissociative S_N2 mechanism. The product selectivity values (S) for solvolysis of **1** in alcohol/water mixtures were in the range of 0.5 to 1.9, which is also consistent with the proposed unimolecular ionization mechanism.

Key Words : Piperonyloyl chloride, Extended Grunwald-Winstein equation, S_N1 mechanism, Solvent kinetic isotope effect, Product selectivity

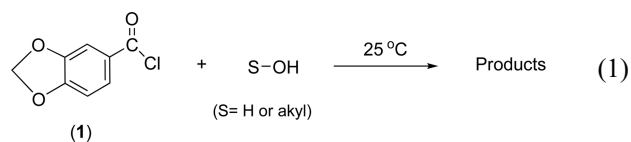
Introduction

The bimolecular solvolysis of acyl halides (RCOX) is believed to proceed either through a concerted S_N2 mechanism or through an addition-elimination (A-E) mechanism involving a tetrahedral intermediate (Scheme 1).¹ For acyl halides with a strong electron donating group (R), a dissociative mechanism involving an acylium ion (RCO^+) intermediate has also been found to be involved.^{1(b),2,3} The three types of mechanism, concerted S_N2 , stepwise ionization S_N1 , and stepwise addition-elimination S_{AN} , are also common in the bimolecular aminolysis of acyl halides.^{1(b),3}

The mechanisms of the acyl-transfer displacement reactions have been intensively investigated both experimentally⁴ and theoretically⁵ for many years. However, the mechanisms of most of these reactions remain not well established, especially for electron-rich acyl transfer reactions.

In order to obtain further understanding of the electron-rich acyl transfer mechanism, a kinetic study of the solvo-

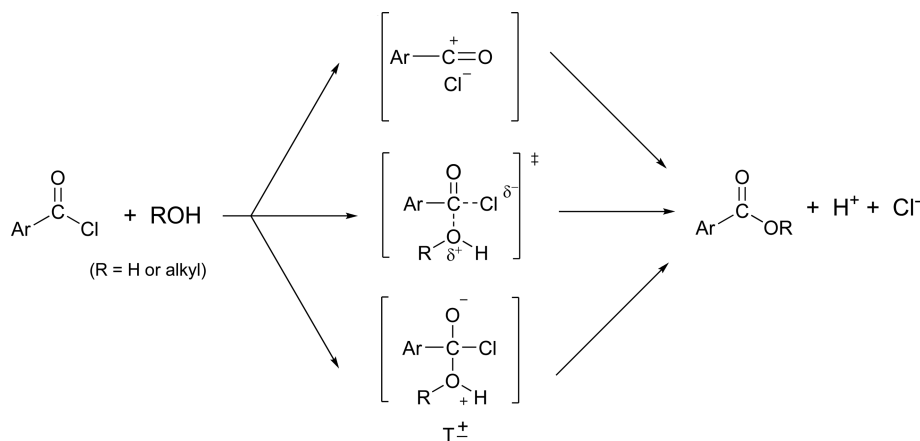
lysis of piperonyloyl chloride (**1**) (Eq. 1) in a variety of pure and binary solvents at 25.0 °C was undertaken. Furthermore, the l , m , and h values were determined using the extended Grunwald-Winstein equations [Eqs. (2) and (3)];⁶ we also determined the enthalpies and entropies of activation, the value of the solvent kinetic isotope effect (SKIE), and the product selectivity (S).



$$\log(k/k_o) = l N_T + m Y_{Cl} \quad (2)$$

$$\log(k/k_o) = l N_T + m Y_{Cl} + hI \quad (3)$$

In Eq. (2), k and k_o represent the rate constants of solvolysis in a given solvent and in a standard solvent (80% ethanol), respectively; l represents the sensitivity to changes in the solvent nucleophilicity (N_T),⁷ and m represents the



Scheme 1

sensitivity to changes in the solvent ionizing power (Y_X , for a leaving group X);⁸ in Eq. (3), h represents the aromatic ring parameter (I).⁹

Results and Discussion

The rate constants (k) for the solvolysis of **1** in 24 solvents were determined at 25.0 °C. The solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, and 2,2,2-trifluoroethanol (TFE). The rate constants are presented in Table 1, together with the solvent nucleophilicity (N_T),⁷ solvent ionizing power (Y_{Cl}),⁸ and aromatic ring parameter (I)⁹ values.

In the present study, the rate constants of the solvolysis, represented in Eq. (1), were measured using an automatic conductivity apparatus. In most solvents, the reactions proceeded rapidly, which enabled the responses to be recorded as a function of time.^{1(b),10} In order to promote a rapid dissolution in the solvent, the substrate was added as a small volume of a concentrated stock solution in acetonitrile; the concentration of the solution was 0.1% acetonitrile.^{1(b),10} The

Table 1. Rate constants for the solvolysis (k/s) of **1**^a in binary solvent mixtures at 25 °C and the N_T , Y_{Cl} , and the I values for the solvent

Solvent ^b (%)	N_T^c	Y_{Cl}^c	I^c	k
100EtOH	0.37	-2.52	0.20	4.86×10^{-4}
90EtOH	0.16	-0.94	-	1.85×10^{-3}
80EtOH	0.00	0.00	0.00	5.72×10^{-3}
70EtOH	-0.20	0.78	-	1.56×10^{-2}
60EtOH	-0.39	1.38	-0.15	4.27×10^{-2}
50EtOH	-0.58	2.02	-	8.17×10^{-2}
40EtOH	-0.74	2.75	-0.24	3.30×10^{-1}
30EtOH	-0.39	3.53	-	6.52×10^{-1}
100MeOH ^d	0.17	-1.17	0.41	4.89×10^{-3}
90MeOH	-0.01	-0.18	-	1.13×10^{-2}
80MeOH	-0.06	0.67	0.14	3.02×10^{-2}
70MeOH	-0.40	1.46	-	9.46×10^{-2}
60MeOH	-0.54	2.07	-0.02	2.13×10^{-1}
50MeOH	-0.57	2.70	-	4.89×10^{-1}
90Acetone	-0.35	-2.39	-0.25	9.07×10^{-5}
87Acetone	-0.34	-1.81	-	1.87×10^{-4}
80Acetone	-0.37	-0.83	-0.23	6.57×10^{-4}
75Acetone	-0.39	-0.28	-	1.56×10^{-3}
63Acetone	-0.54	0.62	-	9.04×10^{-3}
60Acetone	-0.52	1.00	-0.28	1.42×10^{-2}
52Acetone	-0.68	1.45	-	4.00×10^{-2}
42Acetone	-0.81	2.21	-	1.74×10^{-1}
40Acetone	-0.81	2.46	-0.35	1.66×10^{-1}
97TFE ^e	-3.30	2.83	0.49	8.51×10^{-2}

^aUnless otherwise indicated, a 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, containing 0.1% CH₃CN. ^bOn a volume-volume content at 25.0 °C, and the other component is water. ^cValues from refs. 7, 8. ^dValues of $k = 4.36(\pm 0.03) \times 10^{-3} \text{ s}^{-1}$ in deuterated methanol (MeOD), corresponding to $k_{\text{MeOH}}/k_{\text{MeOD}}$ value of 1.12 (with associated standard error).¹¹ ^eSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water. values from literature for related substrates.

rate constants were increased as the amount of water in the binary solvent systems was increased, as shown in Table 1; that is, faster solvolysis reactions took place in the electrophilic (higher ionizing power) solvent systems and slower reactions took place in the nucleophilic solvents. The first-order rate constants increase as the ionizing power Y changes from a lower value to a higher one, *i.e.*, k_1 increases from 0.00486×10^{-1} to $6.52 \times 10^{-1} \text{ s}^{-1}$ as Y changes from -2.52 (100% EtOH) to 3.53 (30%MeOH-70%H₂O).⁸ This means that the rate is highly affected by the solvent with higher ionizing power, Y , suggesting that bond breaking in transition state is the rate limiting step. This phenomenon supports the idea that the solvolysis of **1** is dominated by a unimolecular ionization reaction mechanism.

In deuterated methanol (MeOD), an SKIE ($k_{\text{MeOH}}/k_{\text{MeOD}}$) of 1.16 was observed at 25.0 °C. Also, the values of $k = 4.89 \times 10^{-1} \text{ s}^{-1}$ in 50% MeOH-50% H₂O and $k = 4.36 \times 10^{-1} \text{ s}^{-1}$ in 50% MeOD-50% D₂O corresponded to SKIE values of 1.12. These values are within the range of SKIE values of ~1.2 that were reported for the corresponding solvolyses of *p*-methoxybenzyl chloride,¹² cinnamyl chloride,¹³ *p*-methoxybenzoyl chloride,¹² and 1-piperidinecarbonyl chloride¹⁴ at 25.0 °C, in which the reactions were believed to be S_N1 in character.¹⁵

The extended Grunwald-Winstein equation [Eq. (2)] is useful for determining the extent of nucleophilic participation in the solvent because the magnitudes of l and m in Eq. (2) are the indicators used to determine whether a nucleophilic substitution reaction proceeds through a unimolecular, S_N1 (*i.e.*, $l \approx 0$ and $m \approx 1$), or a bimolecular reaction (S_N2, *i.e.*, $l \approx 1.3$ and $m \approx 0.5$) and an addition-elimination mechanism (*i.e.*, $l \approx 1.6$ and $m \approx 0.7$). Therefore, the determination of the l and m values will provide valuable information concerning the structure of the transition state for the solvolyses.^{1,6,16} The application of the extended

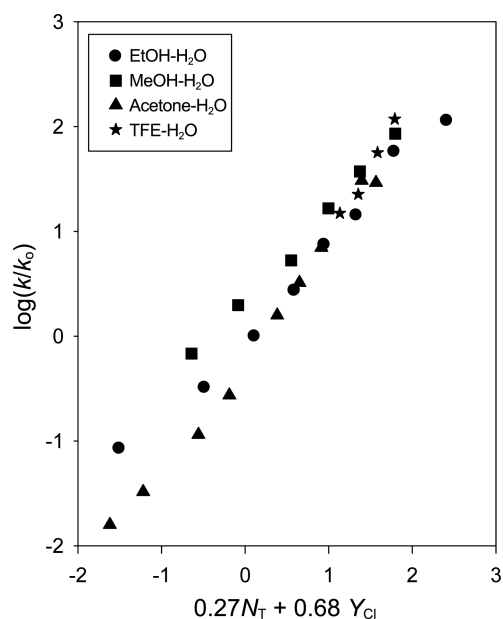


Figure 1. Extended Grunwald-Winstein plot for solvolyses of **1** at 25.0 °C against $0.27N_T + 0.68Y_{Cl} + 0.12$ at 25 °C ($r = 0.954$).

Table 2. Coefficients from the extended Grunwald-Winstein correlations of the specific rates for the solvolysis of **1** at 25.0 °C and a comparison with coefficients from the correlations for other substrates

Substrate	n^a	l^b	m^b	l/m	R^c
2-AdOCOCl ^d	19	~0	0.47±0.03	~0	0.970
C ₆ H ₅ CH=CHCH ₂ Cl ^e	23	0.23±0.07	0.88±0.04	0.26	0.992
<i>p</i> -CH ₃ OC ₆ H ₄ COCl ^f	37	0.31±0.05	0.81±0.02	0.38	0.941
<i>i</i> -PrOCOCl ^g	20	0.28±0.05	0.52±0.03	0.54	0.979
EtSCOCl ^h	19	0.66±0.08	0.93±0.03	0.71	0.982
C ₆ H ₅ S(C=S)Cl ⁱ	20	0.69±0.05	0.95±0.03	0.72	0.987
(CH ₃) ₂ NSO ₂ Cl ^j	32	1.20±0.04	0.72±0.03	1.7	0.985
CH ₃ SO ₂ Cl ^k	43	1.20±0.05	0.52±0.03	2.3	0.969
(CH ₃ O) ₂ PSCl ^l	28	1.16±0.08	0.55±0.03	2.1	0.966
CH ₃ OCOCl ^m	19	1.59±0.09	0.58±0.05	2.7	0.977
C ₆ H ₅ OCOCl ⁿ	21	1.68±0.10	0.57±0.06	3.0	0.973
1 ^o	27	0.30±0.05	0.66±0.02	0.45	0.954

^aNumber of solvents. ^bFrom Eq. (2) and with associated standard error. ^cMultiple correlation coefficient. ^dReference 1(a). ^eReference 13. ^fReference 12. ^gReference 18. ^hReference 24. ⁱReference 20. ^jReference 21. ^kReference 21. ^lReference 21. ^mReference 21. ⁿReference 9(c). ^oThis work.

Grunwald-Winstein Eq. (2)⁶ to the rate constants of the solvolysis of **1** (from Table 1) leads to a good correlation with N_T and Y_{Cl} (correlation coefficient of 0.943 for 27 solvents) with values of 0.27 ± 0.05 for l and 0.68 ± 0.02 for m . This relationship is presented graphically in Figure 1. The sensitivity values (l and m) are reported in Table 2, in which they are compared with values from the literature for related substrates. The application of the extended Grunwald-Winstein Eq. (3)⁶ to the rate constants of the solvolysis of **1** leads to an improved correlation with N_T , Y_{Cl} , and l (correlation coefficient of 0.983 for 15 solvents), with values of 0.30 ± 0.05 for l , 0.71 ± 0.02 for m , and 0.60 ± 0.02 for h . This relationship is presented graphically in Figure 2.

The l value of 0.27 and m value of 0.68 for the solvolysis **1** were similar to those values reported recently for reactions (entries 2-5 in Table 2) that proceed through a unimolecular ionization mechanism,^{1,14-18} whereas these values were different from values reported for bimolecular solvolyses of other substrates (entries 6-10 in Table 2).¹⁹⁻²¹ This suggests that there is a dissociative S_N2 or S_N1 ionization mechanism involving an electrophilic attack by the solvent on the chloride atom of **1**. The solvolysis of **1** features bond breaking ($m = 0.68$) that is much more progressed than the bond making ($l = 0.27$).^{1,13,15-18,24} The higher h value of 0.60 for the solvolysis of **1** was similar to values recently reported for solvolytic reactions of benzyl halides, which are known to proceed through a unimolecular ionization mechanism. This

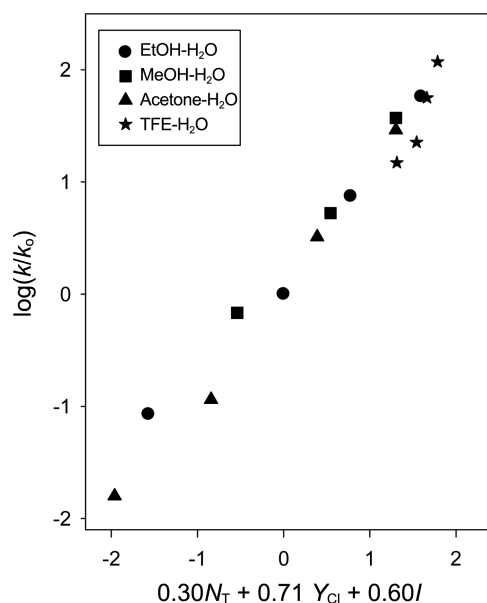
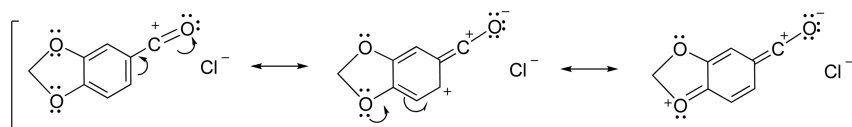


Figure 2. Extended Grunwald-Winstein plot for solvolyses of **1** at 25.0 °C against $0.30N_T + 0.71Y_{Cl} + 0.60l$ ($r = 0.961$).

means that the carbonyl cation can participate in π -conjugation with the adjacent aromatic benzene ring in the ion pair intermediate (Scheme 2).^{6(g),6(h),9(a),22,23}

The l to m ratios have also been suggested as useful mechanistic criteria. The l/m values from the extended Grunwald-Winstein equation can be classified into two types of mechanism: l/m values of 1.2 to 3.5 for the bimolecular mechanism (S_N2) or an addition-elimination pathway (A-E); and l/m values below 0.7 for an ionization pathway (I).⁶ For the solvolysis of **1**, the l/m value was 0.40, which is similar to values determined in previous studies investigating the solvolyses of *p*-methoxybenzoyl chloride,¹² isopropyl chloroformate,¹⁸ and ethyl thiochloroformate;²⁴ these similarities suggest the existence of an S_N1 ionization mechanism (I).

In addition, the $k_{40\%EtOH}/k_{97\%TFE}$ ratio has also been suggested as a useful mechanistic criterion.^{6(b),21} Values of $k_{40\%EtOH}/k_{97\%TFE} > \sim 100$ are considered to represent the bimolecular S_N2 and/or addition-elimination (A-E) pathway. In contrast, several $k_{40\%EtOH}/k_{97\%TFE}$ values were reported for the proposed unimolecular S_N1 reaction or ionization pathway: the solvolyses of diphenyl chloromethane,^{12,25} *p*-methoxybenzyl chloride,¹² cinnamyl chloride,¹³ 1-chloro-1-phenylethane,^{23,26} 4-chloro-4-methyl-2-pentyne,^{22(a)} *trans*-4-chloro-2-pentene,^{22(a)} *tert*-butyl chloride,^{6(c),23} and 1-piperidine-carbonyl chloride¹⁴ (See Table 3). Small values ($k_{40\%EtOH}/k_{97\%TFE} = 0$ to ~ 25) were observed due to the two solvents having the same Y_{Cl} value, *i.e.*, the same degree of solvent assistance for bond cleavage, but different nucleophilicity,



Scheme 2

Table 3. Values of rate ratios in 40% EtOH/H₂O compared with 97% TFE/H₂O at 25 °C

Substrates	$k_{40\text{EtOH}}/k_{97\text{TFE}}$	Substrates	$k_{40\text{EtOH}}/k_{97\text{TFE}}$
	0.18 ^a		2.0 ^e
	0.70 ^b		7.1 ^f
	1.5 ^c		11 ^g
	1.9 ^d		17 ^h

^aReferences 11, 25. ^bReferences 12. ^cReferences 13. ^dReferences 22(a). ^eReferences 23, 26. ^fReferences 22(a). ^gReferences 6(c), 33. ^hReferences 14.

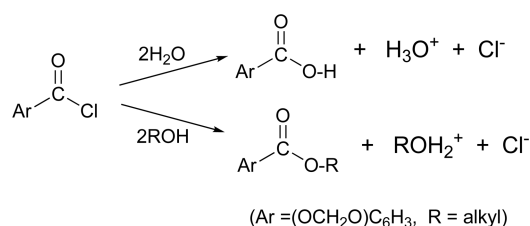
which provides a measure of the minimum extent of nucleophilic assistance.^{6(b),23} The $k_{40\% \text{EtOH}}/k_{97\% \text{TFE}}$ value of 3.88 obtained for the solvolysis of **1** is similar to those values obtained for the eight substrates that are believed to proceed through the S_N1 ionization mechanism (I) (See Table 3).

The reaction of benzoyl chlorides with water produces two equivalents of strong acid, whereas the reaction with an alcohol produces only one equivalent of strong acid, as shown in Scheme 3. If a water-alcohol solvent is used, the reaction, as presented in Scheme 3, is simplified in that the second solvent molecule, which is used to extract the proton from the molecule serving as the nucleophile, could be either water or alcohol. Furthermore, the amounts of each of the two protonated solvent species shown are determined *via* a rapid equilibration within the mixed solvent.

The partitioning ratio ([ester]/[acid]) is used in conjunction with the molar composition ratio for the solvent involved ([H₂O]/[SOH]) in order to calculate the selectivity value (*S*), defined as in Eq. (3).^{17(d),27}

$$S = \frac{([\text{Ester in product}]/[\text{Acid in product}])}{\times ([\text{Water in solvent}]/[\text{Alcohol in solvent}])} \quad (4)$$

The values for the percentages of reactions proceeding with ester formation (×%) for solvolyses of **1**, at 25.0 °C, in mixtures of water with ethanol and methanol are reported in Table 4. The product ratios (×/100 – ×) were then used in Eq. (4) to provide the *S* values, which are also presented in Table 4. The selectivity increases with increases in the water content in the aqueous ethanol and methanol mixtures; thus, the reactivity-selectivity principle (RSP)²⁸ is not followed in

**Scheme 3****Table 4.** Selectivities (*S*) for the solvolyses of (**1**) in alcohol/water mixtures (after one half-life at 25.0 °C)^a

Alcohol ^b %(v/v)	EtOH-H ₂ O		MeOH-H ₂ O	
	[Ester]/[Acid]	<i>S</i>	[Ester]/[Acid]	<i>S</i>
90	1.50	0.54	1.79	0.45
80	0.903	0.73	1.42	0.80
70	0.572	0.79	1.07	1.0
60	0.363	0.78	0.956	1.4
50	0.245	0.79	0.667	1.5
40	0.172	0.83	0.475	1.6
30	0.114	0.87	0.323	1.7
20	0.0670	0.87	0.190	1.7
10	0.0320	0.93	0.0930	1.9

^aDetermined by duplicate HPLC analyses of two solutions of each solvent composition; average deviation < ± 2%. ^bVolume/volume basis at 25.0 °C. ^cInjected 10 μL of a 1% solution of **1** in dry acetonitrile into 3 mL of solvent.

ethanol and methanol mixtures. The smaller value of *S* in the more aqueous media for **1** is a strong indication that the role of alcohol as an electrophile is important, while the effect of the ionizing power is significant in the product-determining step of the reaction of **1**. Similar selectivity changes have been shown to be typical for a unimolecular ionization mechanism channel in aqueous alcohol media.^{12,17(b),(i),25}

Conclusions

The application of the extended Grunwald-Winstein Eq. (2) to the solvolysis of **1** led to an *l/m* value of 0.40. This value was very similar to those reported for reactions that proceed through an ionization mechanism (*l/m* = 0 to ~0.70, Table 3). Therefore, it can be concluded that the solvolysis of **1** proceeds through an S_N1 mechanism, in which the bond breaking is more advanced than the bond formation in the transition-state, determined according to the magnitudes of *l* and *m*.³ The higher *h* value of 0.60 for the solvolysis of **1** indicates that the carbonyl cations were π-conjugated with an adjacent aromatic benzene ring in the ion pair intermediate (Scheme 2) This conclusion can be further supported by considering the solvent kinetic isotope effect (< 1.20) and the lower value of $k_{40\% \text{EtOH}}/k_{97\% \text{TFE}}$ (= 3.88). The selectivity values (*S*) obtained in the binary solvents were also consistent with the proposed mechanism.

Experimental

The solvents were purified as previously described.²⁹ The piperonyl chloride (**1**, Aldrich, 98%) was used as received. The kinetic experiments were performed by allowing a conductivity cell containing 5.0 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. Then, a 10 μL portion of a 1.0 mol dm⁻³ stock solution of **1** in acetonitrile was added. The monitoring of the conductivity increases with time and the rate constant calculations were conducted as previously reported.²⁹ Multiple regression

analyses were performed using commercially available packages.²⁹

The solvolysis products, (ester and acid), were determined via the HPLC analysis, as reported previously,^{6(b),30} the product selectivities, (*S*), were calculated using Eq. (3). The *S* values were calculated from the observed peak area ratios of the ester and acid; *S* values were divided by the appropriate response factor. For the response calibrations, the area ratios from the solvolysis of **1** in pure alcohol and in 40% acetonitrile-water mixtures were used. The eluent was a 60% methanol-water mixture; the flow rate was adjusted to 1 mL min⁻¹. The HPLC system was a Hewlett-Packard 1050 Series instrument, with 250 × 4 mm Spherisorb ODS reversed columns.

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