about 5% of the probe remains in the water phase. This result, which is significantly smaller than the reported 15%,² is similar to that obtained in the present work.

The partition coefficient between a normal hydrocarbon and water has been determined by Hautala and Turro, who have reported a value of 2500.1 We have obtained a similar value, and we have shown that addition of 0.1 M ZnSO_4 only modifies this value in approximately 20%. The analysis carried out previously^{1,2} indicates that nearly 15% of the probe would remain in the water phase at 10^{-2} M CTAB if the micelle behavior were similar to a hydrocarbon solvent. Comparison of this value with those found in the present work shows that there exists an excess of probe incorporated to the micelle (by a factor of nearly 3) relative to that expected if only the dissolution in the core were considered.

The partition between CTAB micelles and water have also been measured by the total solubilization method.^{3,10} The proportion of naphthalene remaining in the water phase was, at 10^{-2} M CTAB, 7% (ref 3) and nearly 10% (ref 10), and the average number of probe molecules by micelle was estimated as 3 and $20.^{3,10}$ Under these conditions, the distribution constant can be different from that estimated at occupancies below 1, but the results obtained also indicate an excess of probe inside the micelle that can be attributed to adsorption on the surface.³ Algrem et al.³ have estimated that at least 20% of the naphthalene molecules solubilized in the micelles are located at the surface. The value that can be estimated from our results, as well as from the reevaluation of the data of Van Bockstaele et al., would indicate that at low occupancies the proportion of probe in the surface must be considerably larger. This result is similar to that observed by Mukerjee and Cardinal when benzene is used as probe¹¹ and can be explained in terms of a larger proportion of probe adsorbed in the surface at low occupancies. We can conclude then that under all of the conditions so far considered (low occupancies both with and without added electrolytes, and at the saturation point) the amount in the micelle is larger than that expected from its partition between normal hydrocarbons and water. The present results can then be explained in terms of the two-state model of solubilization and the interfacial activity of aromatic solutes at hydrocarbon-water interfaces.^{11,12}

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Reaction of *p*-Nitrophenyl Diphenyl Phosphate in Cetyltrimethylammonium Fluoride. Apparent Failure of the Pseudophase Model for Kinetics

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The reaction of \mathbf{F}^- with p-nitrophenyl diphenyl phosphate (pNPDPP) is very rapid in aqueous solutions of cetyltrimethylammonium fluoride (CTAF). However, the results do not conform to the pseudophase ion-exchange model because the rate constant does not become constant when the substrate is fully micellar bound, but continues to increase with increasing [CTAF] or with addition of NaF. Added Br- as NaBr or CTABr inhibits reaction showing that Br⁻ displaces F⁻ from the micelle. Reasons for the apparent failure of the pseudophase model are considered.

Rate surfactant profiles for micellar-catalyzed bimolecular reactions of nonionic reactants in water can be explained unambiguously in terms of reactant distribution between aqueous and micellar pseudophases.²⁻⁴ The situation is more complex for ionic reactions where the distribution of ions between the two pseudophases generally cannot be measured directly. Micellar catalysis of ionic bimolecular reactions is almost always retarded by added salts which contribute counterions that compete with reactive ions for the micelle, and the inhibition increases with

decreasing hydrophilicity of the added ions.^{5,6} However, it has also been suggested that added ions reduce micellar catalysis by reducing the surface potential of the micelle.^{7,8} Some workers have treated the phenomena in terms of one or other of these effects; others have combined them in the treatment.^{2,7,8} Micellar effects on acid–base equilibria have also been discussed in terms of these models.^{9,10}

One method of exploring the different approaches is to eliminate the complications caused by a mixture of counterions by using reactive counterion surfactants whose micelles contain only the reactive counterion. Such surfactant types include $RSO_3^-H^+$ (1); $R^+NMe_3OH^-$ (2); $RN^+Me_3CN^-$ (3); $RN^+Me_3Br^-$ (4), where the ionic reactant is the hydrogen ion or a nucleophilic anion, and R is an alkyl or arylalkyl group.

There is considerable evidence that ca. 70% of the head groups in ionic micelles are neutralized by counterions. which are part of the kinetic micelle, and that the extent of neutralization, β , is insensitive to the nature or con-centration of most counterions.^{6,11} Therefore, provided that the volume of the Stern layer remains constant, the concentration of reactive counterion in the micellar Stern layer will also be constant, and reaction rates should become constant once all the substrate is micellar bound. This behavior has been observed for reactions involving the hydrogen ion in solutions of 1,¹² and of cyanide¹³ or bromide¹⁴ in solutions of 3 and 4, respectively. However, the expected pattern was not found for hydroxide ion reactions in solutions of 2.12 Instead reaction rates increased steadily with increasing surfactant concentration and moreover increased sharply on addition of OH-, even when the substrate appeared to be fully micellar bound.

These results suggest that the simple model is satisfactory for anions which are not very hydrophilic, e.g., $CN^$ and Br^- , but not for the very hydrophilic hydroxide ion. Fluoride ion is also very hydrophilic, and its reaction with *p*-nitrophenyl diphenyl phosphate (pNPDPP) is catalyzed by micellized quaternary ammonium bromides.¹⁵

 $(PhO)_2PO \cdot OC_6H_4NO_2 + F^- \rightarrow$

$$(PhO)_{2}PO \cdot F + OC_{6}H_{4}NO_{2}$$

Our aim was to examine this reaction in micelles of cetlytrimethylammonium fluoride (CTAF). Because pNPDPP is very strongly incorporated in cationic micelles,⁴ the simple model predicts that the first-order rate constant, k_{ψ} , should become constant at relatively low [CTAF]. We did not observe this simple behavior but saw a pattern similar to that found for aromatic nucleophilic substitution by hydroxide ion in micellized surfactant, 2.^{12,16}

Experimental Section

Materials. p-Nitrophenyl diphenyl phosphate (pNPDPP) and CTABr were prepared or purified by methods described elsewhere.¹⁵ Triphenylphosphine (5) was recrystallized from hot water.

Cetyltrimethylammonium fluoride was prepared from CTABr (25 g) by dissolving it in sufficient MeOH to give a clear solution and by adding a 1.5-fold excess of AgF. This general method has been used by Muller and coworkers for the preparation of ω -trifluoroalkyltrimethylammonium fluorides but with an aqueous solution.¹⁷ The mixture was sonicated for ca. 2 h to disperse the AgF and then filtered. The filtrate was tested for Br⁻ (HNO₃/ AgNO₃) and additional AgF was added if necessary.

The solution was concentrated and CTAF was precipitated by addition of Et_2O . This solid was purified by dissolving it in MeOH and adding sufficient Et_2O to induce crystallization. The absence of silver ions was shown by adding NaClO₄ to precipitate the quaternary ammonium ion and by adding NaI to the filtrate. Providing that the product contained neither Br⁻ nor Ag⁺ it was recrystallized (MeOH/Et₂O) and dried (P₂O₅ in vacuo at 64 °C).

The critical micelle concentration (cmc) was 2.1×10^{-3} M, estimated by the surface tension method,¹⁸ and there was no minimum in a plot of surface tension against log [CTAF]. The cmc is larger than that of the chloride and bromide. Critical micelle concentrations generally decrease with decreasing hydrophilicity of the counterion.¹⁸



Figure 1. Rate of reaction of *p*-nitrophenyl diphenyl phosphate at pH 9.0, 25.0 °C in CTAF: (•) 10^{-3} , (O) 3×10^{-3} , (=) 10^{-2} M borate.

Kinetics. The reaction was followed under the conditions similar to those used earlier for dephosphorylation in CTABr + NaF,¹⁵ viz., 25.0 °C and pH 9.0 (borate buffer). The substrate was added (4 μ L in MeCN) to 3 mL of the reaction medium, giving a substrate concentration of ca. 2 × 10⁻⁵ M.

The formation of *p*-nitrophenoxide ion was followed at 400 nm on a Gilford spectrophotometer and the kinetics were cleanly first order. The rate constant, k_{ψ} , is in reciprocal seconds.

Micellar Incorporation. The binding constants, K_{s}^{19} of a chemically inert solute, triphenylphosphine oxide (5), to the micelles were estimated from the solubilities of 5 in solutions of CTABr and CTAF. The solute concentrations were estimated from the absorbance at 260 nm of solutions to which EtOH was added to break up the micelles. (The final solution was 90:10 v/v EtOH:H₂O.) As predicted the solubilities varied linearly with [CTAF] and [CTABr] for surfactant concentrations above the cmc and up to 10^{-1} M. The values of K_s were 680 and 430 M⁻¹ for CTAF and CTABr, respectively.

These results suggest that values of K_s for micellar binding of hydrophobic solutes are similar for CTAF and CTABr. In CTABr solutions K_s for pNPDPP is ca. 2 × 10⁴ M⁻¹.²⁰

Results

Reaction in CTAF. The rate constants, k_{ψ} , increase steadily with increasing CTAF (Figure 1), and, although we cannot measure the binding constant of pNPDPP to micellized CTAF, comparison with the micellar binding of triphenylphosphine oxide (Experimental Section) suggests that the substrate should be fully bound at relatively low [CTAF]. An increase in the concentration of the borate buffer slightly decreases the rate, probably because borate competes with fluoride ion for the micelle. The effect is small relative to the overall rate enhancement by CTAF, and similar effects of borate ion were observed for reactions in mixtures of CTABr and NaF.¹⁵ These observations suggest that borate ion does not bind strongly to cationic micelles.

In the absence of surfactant the second-order rate constant for reaction of fluoride ion is ca. 0.1 $M^{-1} s^{-1}$ at 25.0 °C,¹⁵ so that the reaction in 7 × 10⁻³ M CTAF (Figure 1) is as fast as that in 1 M NaF. Another basis for comparison is the rate in 10⁻² M NaF at the optimum concentration of CTABr (0.002 M)¹⁵ where $k_{\psi} = 0.0027 s^{-1}$ as compared with 0.12 s⁻¹ in 10⁻² M CTAF (Figure 1). Thus CTAF is a very effective dephosphorylating agent as compared with fluoride ion in water or in the presence of CTABr. A similar situation was found for aromatic nucleophilic



Figure 2. Effect of added fluoride ion on reaction at pH 9.0, 10^{-3} M borate at specified [CTAF].

TABLE I: Effect of Added NaF^a

		[CTAF], M		
[NaF], M	0.001	0.01	0.04	
0.05 0.09 0.20	0.015 ^b 0.20	0.13 0.28 0.29 0.33	0.20 ^b 0.30	

^a Values of k_{Ψ} , s⁻¹ in 10⁻³ M borate buffer at 25.0 °C. ^b Interpolated values.

substitution in solutions of micellized $2.^{12}$

Effect of Added Fluoride Ion. Added F^- increases k_{ψ} even when the substrate appears to be fully micellar bound. The rate enhancement is much too large to be explained in terms of reaction in the aqueous pseudophase, cf. ref 12.

The rate does not increase linearly with added NaF, and there appears to be a saturation effect, as is shown by the variation of k_{ψ} with [NaF] for various [CTAF] (Figure 2). In addition the rate enhancement by NaF appears to be largest at the lowest [CTAF] (Table I and Figure 2). Added salts typically decrease the cmc,¹⁸ so that NaF should increase the amount of micellized surfactant, but this effect will be unimportant when [CTAF] \gg cmc, which is the situation in most of the conditions illustrated in Table I and Figure 2.

Effect of Added Bromide Ion. Added bromide ion slows the reaction of fluoride ion with pNPDPP in CTABr,^{5,12} and we see very similar results here whether bromide ion is added to CTAF as NaBr or as CTABr (Table II). The inhibition is not large when fluoride is in large excess over bromide ion; but is very marked when the concentrations of the two ions are similar. These effects are consistent with the counterion competition model for negative salt effects on micellar-catalyzed bimolecular reactions.^{5,6} The rate effects are not related in any simple way to the ionic strength of the solution but show that bromide competes very effectively with fluoride ion for the cationic micelle.

The inhibition clearly depends upon the ratio of total fluoride to bromide ion, and not upon the relative amounts of CTAF and CTABr, as is shown by the effect of added NaF upon the rate constants in mixtures of CTAF and NaBr (Table II).

Discussion

Anomalous Rate Effects in Relative Counterion Micelles. The failure of the simple kinetic model appears to depend upon the hydrophilicity of the anionic nucleophile. For example rate-surfactant plateaux are obtained for

TABLE II: Effect of Added Bromide Ion^a

[NaF], M	[CTABr], M	[CTAF], M			
		0.01	0.03	0.05	
	· · · · · · · · · · · · · · · · · · ·	0.13	0.18	0.22	
0.001		0.12			
0.003			0.16		
0.005		0.059		0.20	
0.010		0.123^{b}		0.20^{b}	
	0.01	0.050			
0.015			0.087		
0.025				0.092	
	0.05			0.072	
0.10	0.00	0.014^{b}	0.012^{b}	0.020	

^a Values of k_{Ψ} , s⁻¹ in 10⁻³ M borate at 25.0 °C.

 b [CTAF] + [NaF] = 0.1 M.

reactions of CN⁻ and Br⁻ in CTACN and CTABr respectively,^{13,14} but not with reactions in CTAF or R⁺NMe₃-OH.¹² Hydrophilicity of the counterion cannot be the sole cause of the failure because the model successfully describes the rate-surfactant profiles for acetal hydrolysis catalyzed by micellized alkane sulfonic acids.¹² The hydrogen ion may, however, be a special case because it can hydrogen bond, or bind covalently, to the sulfonate head groups of the micelle. Such interactions also explain why hydrogen ion in an anionic micelle appears to be less reactive than in water.^{12,21}

Anions such as F^- , CN^- , or Br^- have no covalent or other directed interactions with a quaternary ammonium head group, so that we need some other explanation for the unusual behavior of hydrophilic anions. Again salt effects on the surface potential of the micelle do not appear to be of direct importance. One could suppose, for example, that an added salt, e.g., NaF, lowers the surface potential of the micelle and reduces the electrostatic stabilization of the transition state, cf. ref 7 and 8, but this interaction would then reduce the rate, whereas added NaF increases the rate (Table I and Figure 2).

Our rate-surfactant profiles for reaction in CTAF + NaF do not fit the simple pseudophase ion-exchange model which assumes that β is constant,⁶ but the results in the presence of Br⁻ accord with it, on the assumption that the two anions compete for the cationic micelle. Similar observations have been made on hydroxide ion reactions which do not follow the simple model when OH⁻ is the only counterion,¹² although reactions of OH⁻ in solutions of CTABr or similar surfactants behave as predicted by a competitive ion-exchange model.^{5,6}

Initially the distribution of counterions about a micelle was described in terms of the Gouy-Chapman model, but a more refined treatment is based on a Stern layer model in which counterions are believed to be sufficiently tightly bound to the micelle as to migrate with it.²³ This model successfully explains micellar effects upon the rates of most reactions.²⁴ However, it fails when the only counterion is OH^- or F^- , so that some other explanation should be sought. For example we could postulate that reaction occurs not only in the aqueous and micellar pseudophases but also across the shear surface at the micelle-water interface. Alternatively, one could suppose that the distribution of hydroxide or fluoride ions about the micelle follows the Gouy-Chapman model so that the probability of reaction between a micellar-bound substrate and the nucleophilic anion depends on the total anion concentration. (These two descriptions are mechanistically equiv $alent.)^{12}$

Another possibility is that solutions of CTAF gives aggregates whose structures cannot be described in terms of a simple equilibrium between monomeric and micellized surfactant.²⁷ However, the variation of surface tension with [CTAF] and the solubilization of triphenylphosphine oxide both follow the expected patterns (Experimental Section), so that these properties give no evidence of any unusual behavior.

There is physical evidence which suggests that ω -trifluoroalkyltrimethylammonium fluorides (6) behave dif-

$$\frac{\text{CF}_{3}(\text{CH}_{2})_{n}\text{N}^{+}\text{Me}_{3}\text{F}}{6, n = 9, 11}$$

ferently from other cationic surfactants. Chemical shifts of micellar counterions depend on surfactant concentration.²⁸ They are typically constant below the cmc, but for surfactant concentrations above the cmc there is a linear relation between the chemical shift and the reciprocal of the surfactant concentration. The breakpoint of these plots is at the cmc, and these observations are consistent with the generally accepted model of counterion binding to the micelle.²⁸ However, solutions of 6 behave anomalously. Plots of the chemical shifts of F⁻ against reciprocal concentrations of 6 are smooth curves with no obvious break point corresponding to the cmc.¹⁷ When KF is added to 6 the chemical shift of the ω -CF₃ group is constant for dilute surfactant, but at higher concentrations plots of chemical shift against reciprocal concentration are either smooth curves or consist of two straight lines of different slopes. This unexpected behavior was described in terms of a double equilibrium model in which monomeric surfactant was in equilibrium with both small and large micelles. However, it was noted that a multiple equilibrium model would also probably fit the data.¹

The ω -trifluoromethyl group may complicate comparison of 6 with CTAF, but is appears that it is the presence of the fluoride counterion which causes the unexpected relation between chemical shift and surfactant concentration.¹⁷ If this anomalous behavior is related to the hydrophilicity of the fluoride ion, as seems reasonable, we would expect, by analogy, that hydroxide ion surfactants^{12,16} also would not fit the simple micellar model, as was found.^{12,16}

An increase in [CTAF] or addition of fluoride ion might affect the reaction rate by changing the micellar slope and size, e.g., from spheroidal to rodlike. However, this explanation seems improbable on several grounds: (i) although micelles of CTABr grow and elongate with increasing concentration²⁹ these changes do not affect rate constants of reactions at the micellar surface;³⁰ and (ii) although micelles of CTABr grow at concentrations greater than 0.05 M it was necessary to go to 0.4 M to observe such growth with CTACl.²⁹ Observations using quasi-elastic light scattering are consistent with these results,³¹ and moreover added NaCl does not have a large effect on micellar growth. Thus a CTAF micelle, with its hydrophilic counterion, would not be expected to grow rapidly with increasing [CTAF] or $[F^-]$.

A double or multiple equilibrium model¹⁷ predicts that the micelles should become more "normal" as we add either the surfactant counterion, e.g., $F^{\scriptscriptstyle -}$ or $OH^{\scriptscriptstyle -},$ or a more hydrophobic counterion such as Br⁻, and this is exactly what we observe (Figure 2, Tables I and II, and ref 12).

The values of k_{ψ} appear to reach a limit of ca. 0.4 s⁻¹ both with increasing [CTAF] and with addition of NaF to CTAF (Figures 1 and 2). A simple model for micellar catalysis of bimolecular reactions, based on an increase of reactant concentration in the Stern layer, suggests that the maximum first-order rate constant, k_{u}^{max} , with fully bound substrate, should be given by eq 1,^{4,20,25} where *n* is the mole

$$k_{\mu}^{\max} \approx 7nk_{w} \tag{1}$$

ratio of the reagent, e.g., F^- , in the micelle and k_w is the second-order rate constant in water, which for our system is $0.1 \text{ M}^{-1} \text{ s}^{-1}$. For a reactive counterion micelle such as CTAF, $n \equiv \beta$, so that if $\beta \approx 0.7$, cf. ref 6, eq 1 predicts a value of k_{ψ}^{\max} of ca. 0.7 s⁻¹, which is only slightly larger than the largest observed values of k_{ψ} (Figures 1 and 2).

The simple treatment based on eq 1 fits rate enhancements of a number of reactions mediated by both nonfunctional and functional micelles⁴ including addition of CN⁻ to N-alkylpyridinium ions in solutions of CTACN.¹³ Thus we see anomalous kinetic behavior in dilute CTAF, and the predicted behavior in more concentrated CTAF. This result is consistent with our hypothesis that surfactants having very hydrophilic counterions, e.g., F⁻ or OH⁻, only form "normal" micelles at relatively high surfactant concentration, and that at low concentration they form smaller aggregates which bind nonionic hydrophobic solutes but do not so effectively bind hydrophilic counterions.

The kinetic evidence suggests that for a situation in which there is a mixture of counterions the kinetic salt effects and rate-surfactant profile are governed by the properties of more hydrophobic counterion. Thus, for reactions of hydrophilic anions, such as hydroxide or fluoride in micelles in which bromide is the predominant counterion, the kinetic behavior is that predicted by the Stern layer ion-exchange model of micellar kinetics, although the model is inadequate for interpretation of rate data when only very hydrophilic counterions are present in low concentration.

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A Quantitative Treatment of Micellar Effects upon Deprotonation Equilibria

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The apparent base dissociation constants, $K_{\rm B}$, for deprotonation of benzimidazole in dilute NaOH go through minima with increasing concentration of cetyltrimethylammonium ion surfactants (CTAX, X = Cl, Br, NO₃) at concentrations above the critical micelle concentration (cmc). However, $K_{\rm B}$ decreases smoothly if the concentration of surfactant counterions is maintained at 0.1 M. In both cases the micellar effect on $K_{\rm B}$ follows the sequence CTACl > CTABr > CTANO₃. These observations are consistent with a pseudophase ion-exchange model in which the micelle binds OH⁻ and both forms of the indicator, increasing deprotonation and decreasing $K_{\rm B}$, but at the same time the counterion of the surfactant displaces OH⁻ from the micellar surface so that $K_{\rm B}$ goes through a minimum with increasing [CTAX]. This model leads to a very simple quantitative treatment which fits the data for [CTAX] > 0.01 M. A similar pattern of behavior has been found for deprotonation of phenols and oximes in CTABr in the presence of borate buffer. Intrinsic basicity constants in the micellar pseudophase can be estimated which are larger than those in water by approximately one order of magnitude.

Indicator equilibria provided the first examples of micellar-induced effects upon chemical reactions in aqueous solution.² Hartley showed, for example, that deprotonation of nonionic indicators was increased by cationic and decreased by anionic micelles,³ and his original conclusions have been supported by recent work.^{4,4}

A successful interpretation must account for some additional observations. (i) Apparent acid dissociation constants, K_A , go through maxima with increasing concentration of cationic surfactant.⁶ (ii) Added salts decrease micellar effects upon acid-base equilibria and the magnitude of the effect increases with decreasing hydrophilicity of added counterion to the micelle.4,5,7

Two models have been used to explain these observations. The first relates the change in apparent acid dissociation constants, $K_{\rm A}$, to surface potential effects on the interfacial pH and the stability of the charged form of the indicator.^{4,8,9} The second, the pseudophase ion-exchange model, places emphasis on the ability of a cationic micelle, for example, to bind OH⁻, and thus to promote deprotonation of a weak acid at the micellar surface.¹⁰ Various workers have shown how either of these models can account qualitatively for micellar effects on acid-base equilibria and reaction rates, and it is difficult to develop quantitative treatments which distinguish between them.^{5,11}

The aim of this work was to apply the pseudophase ion-exchange model, originally developed for micellar effects upon reaction rates, $^{6,10-15}$ to equilibria, and we have examined deprotonation of benzimidazole, phenols, and oximes in alkaline media. Our basic assumption is that there will be a competition between OH⁻ and other anions, micellar bound indicator and the availability of OH⁻ in the micellar pseudophase. Maxima in K_A are explained in terms of two opposing effects. (i) Cationic micelles bind OH⁻ and both forms of the indicator, concentrating them in the small volume of

the micellar pseudophase, and therefore shifting the equilibrium in favor of deprotonation. (ii) Additional surfactant "dilutes" the reactants in the increasing volume of the micellar pseudophase. In addition counterions, added as a simple salt, reduce deprotonation by expelling OH⁻ from the surface of the cationic micelle. The relative affinities of the counterions for the cationic micelle are expressed in terms of ion-exchange parameters^{10,15} based on a model which is formally identical with that developed for counterion binding to polyelectrolytes.¹⁶

e.g., Cl⁻, Br⁻, or NO_3^{-} , for the cationic micelles. Thus deprotonation of an indicator at a cationic micellar surface

will depend upon the intrinsic basicity constant of the

Micellar effects upon deacylation by the benzimidazolide anion (1) played a key role in the development of an un-

$$\underbrace{\bigcirc}_{1}^{N} + H_{2} \circ \stackrel{\kappa_{B}}{=} \underbrace{\bigcirc}_{N}^{NH} + OH^{-}$$

derstanding of micellar catalysis,¹³ and therefore we have examined deprotonation of benzimidazole (2). Because we are using an ion-exchange model it is convenient to analyze the micellar effects in terms of the apparent basicity constants, $K_{\rm B}$.

We have also examined deprotonation of phenols and oximes in connection with studies of micellar-catalyzed

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