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Copper-Catalysed Oxidation of Cyanide by Peroxide in Alkaline Aqueous Solution*

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Abstract

The oxidation of cyanide by peroxide in alkaline aqueous solution is catalysed by copper complexes. In the presence of excess cyanide, copper(II) is reduced to form the tricyanocuprate(I) complex. The cyanogen oxidation product is hydrolysed with disproportionation to cyanate and cyanide:

$$2Cu^{II} + 2CN^- \rightarrow 2Cu^I + (CN)_2$$

$$(CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O$$

$$Cu^I + 3CN^- \rightleftharpoons Cu(CN)_3{}^{2-}$$

The stoichiometry and kinetics of the catalysed oxidation have been investigated. Hydrogen peroxide oxidizes coordinated cyanide with a rate that is first order in peroxide and first order in copper but independent of cyanide concentration in the presence of excess cyanide.

$$Cu(CN)_3{}^{2-} + H_2O_2 \rightarrow Cu(CN)_2{}^- + OCN^- + H_2O$$

$$Cu(CN)_2{}^- + CN^- \rightleftharpoons Cu(CN)_3{}^{2-}$$

When the excess cyanide is consumed and $Cu(CN)_2{}^-$ becomes the dominant species, the reaction becomes more complex and less efficient. Under certain conditions the stoichiometry revealed a peroxide-to-$Cu(CN)_2{}^-$ ratio of about 6 : 1, instead of the minimum of 2·5 : 1 required for the oxidation of the coordinated cyanide to cyanate and the Cu^I to $Cu(OH)_2$. This suggests that peroxide is consumed by a copper-catalysed disproportionation, in competition with oxidation of the coordinated cyanide. An intermediate yellow complex forms while peroxide is present, before $Cu(OH)_2$ finally precipitates.

The consequence of this mechanism is that the most efficient process for the destructive oxidation of cyanide has a high cyanide-to-copper ratio, to minimize the final concentration of $Cu(CN)_2{}^-$ which consumes peroxide inefficiently. The rate of the reaction depends on the concentration of copper, however, which must be large enough for a satisfactory turnover.

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Introduction

The detoxification of aqueous cyanide effluent is a continuing technological challenge.[1] In some environments slow photodegradation by sunlight is adequate. In other situations a chemical treatment process is required. Typically hypochlorite has been used to oxidize the cyanide to cyanogen chloride which is hydrolysed to cyanate and chloride. This process suffers from some disadvantages, however, which include the need to control the reaction carefully to avoid release of the toxic cyanogen chloride and the formation of large quantities of salt in the effluent.

The use of peroxide in place of hypochlorite enables direct oxidation to cyanate, which is then hydrolysed to carbonate and ammonia. The reaction requires a catalyst, however, and copper has been found effective for this purpose. Copper also catalyses the decomposition of peroxide, so that some of the oxidant is wasted. The present work was undertaken to investigate the conditions necessary for the efficient use of peroxide for this purpose and to begin an examination of the mechanism of the process.

Experimental

Merck Analysis Grade NaCN, $CuSO_4.5H_2O$ and NaOH were used as received. The H_2O_2 was 3% w/v produced by Drug Houses Australia. Water was singly distilled.

Electronic spectra were recorded with a Beckman Acta V spectrophotometer interfaced to a Hewlett-Packard 9835A computer. Copper analyses were performed by atomic absorption spectroscopy with a Varian-Techtron AA6 instrument.

The concentration of the peroxide was determined by titration with standard $KMnO_4$ solutions.

The concentration of cyanide in solution was measured potentiometrically with an Orion 94-06 cyanide-selective electrode together with an Orion 90-01-00 double-junction reference electrode, connected to an Orion Ionanalyzer 901. The system was calibrated with solutions of 1·0 and 10 ppm NaCN in 0·1 M NaOH.

Cyanate was measured colorimetrically as the dicyanatodipyridinecopper(II) complex.[2] This method has the advantage that cyanide does not interfere. Two extractions with chloroform were used; subsequent extractions did not result in good phase separation. The extracts were combined and diluted to 25 ml with chloroform, and the absorbance was measured at 680 nm.

Results

Copper(II) *with Excess Cyanide*

When a 1·1 mM $CuSO_4$ solution is added to an alkaline solution of 6·9 mM NaCN containing 1 mM NaOH, the colour of the solution changes from the blue of copper(II) to colourless, and the pH drops. The interpretation of these observations is that blue Cu^{II} is reduced to colourless Cu^{I} with the formation of cyanogen [equation (1)],[3] which disproportionates to cyanate and cyanide with the consumption of base [equation (2)]:

$$2Cu^{II} + 2CN^- \rightarrow 2Cu^{I} + (CN)_2 \qquad (1)$$

$$(CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O \qquad (2)$$

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[1] Ritcey, G. M., 'Tailings Management' (Elsevier: Amsterdam 1989).

[2] Martin, E. L., and McClelland, J., *Anal. Chem.*, 1951, **23**, 1519.

[3] Baxendale, J. H., and Westcott, D. T., *J. Chem. Soc.*, 1959, 2347.

Cyanate hydrolyses only slowly in base [equation (3)] with a rate constant k_3 of $1{\cdot}06\times10^{-6}\ \mathrm{s}^{-1}$ at 60°C, independent of base concentration:[4,5]

$$\mathrm{OCN^- + H_2O + OH^- \rightarrow CO_3{}^{2-} + NH_3} \qquad (3)$$

On the other hand, cyanic acid is a weak acid with $\mathrm{p}K_\mathrm{a} \approx 4$ which hydrolyses more rapidly in acid with a second-order rate constant k_4 of $0{\cdot}06\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 18°C:[5]

$$\mathrm{OCNH + H_2O + H^+ \rightarrow CO_2 + NH_4{}^+} \qquad (4)$$

The d^{10} copper(I) ion forms a series of stable, colourless, anionic cyano complexes with some of the properties shown in Table 1.[6–8] This accounts for the generation of the colourless solution described above. This inference is confirmed by the measurement of the spectrum of the colourless solution, which displays a peak maximum at 238 nm, with a small shoulder at 250 nm, consistent with the presence of $\mathrm{Cu(CN)_3{}^{2-}}$ with a small amount of $\mathrm{Cu(CN)_4{}^{3-}}$. The presence of these species is also consistent with calculations based on the equilibrium constants, K_f, which give a composition of 1·0 M $\mathrm{Cu(CN)_3{}^{2-}}$ and 0·1 mM $\mathrm{Cu(CN)_4{}^{3-}}$.

Table 1. Cyanocuprate(I) complexes

Equilibrium	$\log K_\mathrm{f}$	Raman (cm^{-1})	U.v. (nm)	$\log \epsilon$
$\mathrm{Cu^+ + 2CN^- \rightleftharpoons Cu(CN)_2{}^-}$	23·9	2113	223	3·96
			234	3·96
$\mathrm{Cu(CN)_2{}^- + CN^- \rightleftharpoons Cu(CN)_3{}^{2-}}$	5·3	2106	238	4·06
$\mathrm{Cu(CN)_3{}^{2-} + CN^- \rightleftharpoons Cu(CN)_4{}^{3-}}$	1·9	2094	235	4·04
			250	3·55

Oxidation of Ionic Cyanide

When hydrogen peroxide was added to the colourless solution, i.e., so that the initial reagent concentrations were 1·1 mM $\mathrm{CuSO_4}$, 6·9 mM NaCN, 1·0 mM NaOH and 10·4 mM $\mathrm{H_2O_2}$, the solution was colourless for over an hour and then turned yellow. The concentration of ionic cyanide was measured with a cyanide electrode and was found to decrease at a nearly constant rate.

This rate was measured as a function of initial copper and peroxide concentrations. The reaction conditions began with 6·4 mM $\mathrm{CN^-}$ at pH 10·7; the copper concentrations varied between 0·22 and 1·65 mM, and the peroxide concentrations between 6·9 and 20·8 mM. The linear decrease in the cyanide concentration implies that the rate is independent of the cyanide concentration. This is consistent with the large formation constant of $\mathrm{Cu(CN)_3{}^{2-}}$. If only coordinated cyanide is oxidized, then, as long as there is excess cyanide in the solution, the concentration of $\mathrm{Cu(CN)_3{}^{2-}}$ is constant and independent of the ionic cyanide concentration.

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[4] Kemp, I. A., and Kohnstam, G., *J. Chem. Soc.*, 1956, 900.

[5] Jensen, M. B., *Acta Chem. Scand.*, 1958, **12**, 1657.

[6] Sharpe, A. G., 'The Chemistry of Cyano Complexes of the Transition Metals' (Academic Press: London 1976).

[7] Simpson, E. A., and Waind, G. M., *J. Chem. Soc.*, 1958, 1746.

[8] Kappenstein, C., and Hugel, R., *J. Inorg. Nucl. Chem.*, 1974, **36**, 1821.

According to this mechanism the rate should depend linearly on the copper concentration, in the range in which $Cu(CN)_3^{2-}$ is the dominant species. With 6·9 mM CN^- and 10·4 mM H_2O_2, the dependence of the rate on the initial copper concentration could be described by equation (5) (Fig. 1):

$$-d[CN^-]/dt = (9{\cdot}5\pm0{\cdot}4)\times10^{-8}\ \text{M s}^{-1} + ((6{\cdot}5\pm0{\cdot}3)\times10^{-4}\ \text{s}^{-1})[Cu] \qquad (5)$$

The first term is possibly the result of oxidation of another species such as $Cu(CN)_4^{3-}$.

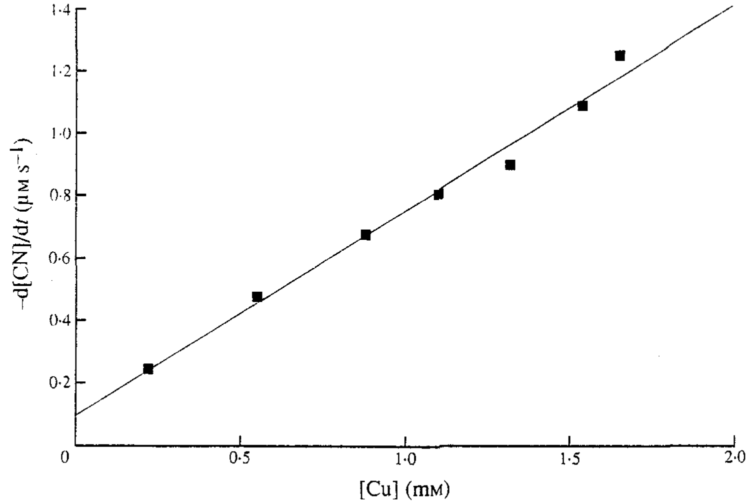

Fig. 1. Rate of disappearance of ionic cyanide as a function of the copper concentration.

The rate of the reaction is also first order in peroxide concentration. For solutions containing 6·9 mM CN^- and 1·1 mM Cu, the rate of ionic cyanide concentration decrease again is linear and is described by equation (6) (Fig. 2):

$$-d[CN^-]/dt = (-3{\cdot}0\pm0{\cdot}5)\times10^{-7}\ \text{M s}^{-1} + ((1{\cdot}11\pm0{\cdot}04)\times10^{-4}\ \text{s}^{-1})[H_2O_2] \qquad (6)$$

The negative first term suggests that there is some parallel, non-productive consumption of peroxide which does not result in any decrease in the ionic cyanide concentration, so that the peroxide concentration must be at least 3 mM before any cyanide is oxidized.

Stoichiometry

At the end of this reaction period the solution turned yellow. The yellow solution slowly decomposed with evolution of a gas over a period of a day to give a green-blue precipitate and a colourless supernatant solution. The precipitate was shown to be predominantly $Cu(OH)_2$, as described below.

The supernatant solution still contained a significant amount of copper which was in the form of $Cu(CN)_2^-$. Fig. 3 illustrates the concentration of copper remaining in the filtrate after separation of the precipitate, as a function of the initial peroxide-to-cyanide ratio. For a solution which initially contained 1·1 mM Cu^{II} and 6·9 mM CN^-, all of the copper remained soluble unless the peroxide-to-cyanide ratio was greater than 0·7 : 1. At these concentrations 2·2 mM CN^- would be used to complex the copper as $Cu(CN)_2^-$ and 0·55 mM to form Cu^I from Cu^{II} [equations (1) and (2)]. This leaves only 60% of the cyanide available

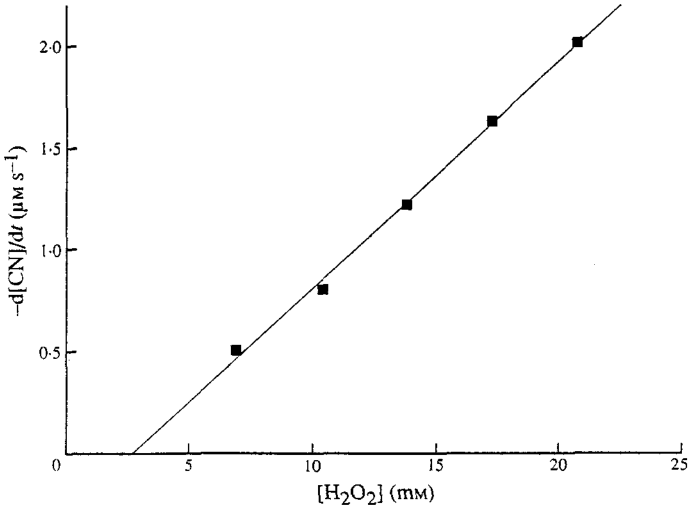

Fig. 2. Rate of disappearance of ionic cyanide as a function of the peroxide concentration.

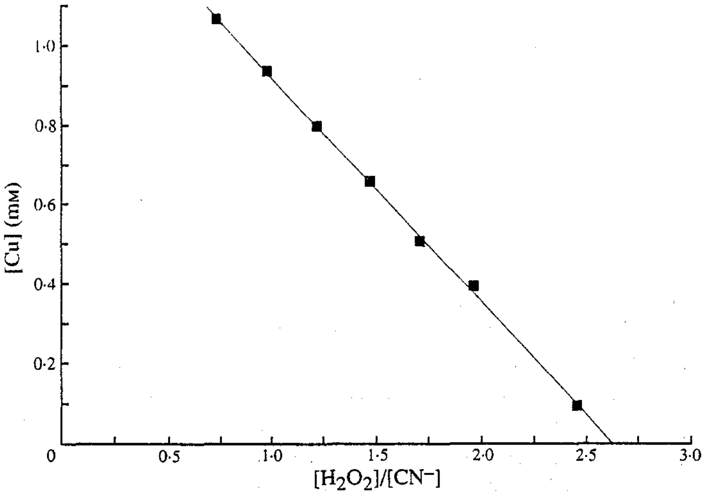

Fig. 3. Copper remaining in solution, in reaction solutions initially with 1·1 mM $CuSO_4$ and 6·9 mM NaCN at pH 11, as a function of the peroxide-to-cyanide ratio.

for initial oxidation by the peroxide, so that a 0·7:1 ratio of peroxide to initial cyanide is sufficient to oxidize this cyanide. That is, of the initial 6·9 mM cyanide, 4·1_5 mM is available for oxidation through formation of $Cu(CN)_3^{2-}$ from $Cu(CN)_2^-$.

This implied stoichiometry of one peroxide to oxidize one cyanide was checked by measuring the ionic cyanide remaining in solution after a deficiency of peroxide had been added. Two experiments were performed with a copper concentration of 0·55 mM and an initial ionic cyanide concentration of 5·2 mM. Addition of 2·1 mM peroxide resulted in depletion of 2·1 mM cyanide, and addition of 3·4 mM peroxide resulted in depletion of 3·4 mM cyanide, these results confirming the 1:1 stoichiometry.

Cyanate was identified as the major oxidation product. The filtrate from a reaction mixture containing 1·1 mM $CuSO_4$, 1 mM NaOH, 6·9 mM NaCN and 21 mM H_2O_2 was analysed for cyanate by the colorimetric method described above. This mixture contained enough peroxide to oxidize all of the cyanide present and to precipitate all of the copper. The filtrate was found to contain 5·2 mM cyanate. This is a minimum value because only two of the four extractions described in the procedure[2] were performed and the cyanate concentration fell in the lower region of the calibration curve.

The identification of $Cu(CN)_2^-$ as the copper species in the colourless filtrate was made spectrophotometrically and by the chemical properties of the filtrate solution. The u.v. spectrum of a 20-fold dilution of the filtrate displayed absorption maxima at 234 and 207 nm with a shoulder at 223 nm, in good agreement with literature values for $Cu(CN)_2^-$. The colourless solution was indefinitely stable, but the addition of more peroxide resulted in a yellow colour within minutes. Addition of acid gave a light blue precipitate which slowly dissolved on standing, consistent with the formation and dissolution of CuCN.

Oxidation of $Cu(CN)_2^-$

As the peroxide-to-cyanide ratio is increased, the cyanide complexed as $Cu(CN)_2^-$ is oxidized and the copper is precipitated. The reaction mixture was allowed to stand overnight and then the very fine precipitate was collected by filtration on 0·22 micron Millipore filters and washed with water. The colour of the precipitate varied from light green at pH 8 to brown at pH 12. The colour was also darker when a higher peroxide-to-cyanide ratio was used. Qualitative tests indicated that there was some peroxide in the precipitate, which amount was the greater with the darker colour. Infrared measurements showed a small peak at 2180 cm^{-1} due to a small amount of cyanide or cyanate.

The precipitation of the copper from the spent product solution is slow and occurs over the period of 10 h or more. During this time the pH of the solution drops. In one experiment in which the pH was monitored during the precipitation, the hydroxide concentration dropped from 1 to 0·15 mM. The amount of copper in the precipitate corresponded to a concentration of 0·5 mM. These observations suggest that the precipitate is largely $Cu(OH)_2$.

The peroxide oxidation of $Cu(CN)_2^-$ is not stoichiometric. The concentration of peroxide required to oxidize a fixed amount of cyanide increases dramatically as the concentration of copper is increased, as illustrated in Fig. 4. In Fig. 4 the amount of copper which remains in the solution as $Cu(CN)_2^-$ is plotted as a function of the initial peroxide concentration for three different initial copper concentrations. As the copper concentration is increased, from the bottom to the top of Fig. 4, the amount of peroxide required to oxidize all of the cyanide and hence precipitate all of the copper increases from 10 to 25 mM, even though each experiment involved only 6·9 mM cyanide.

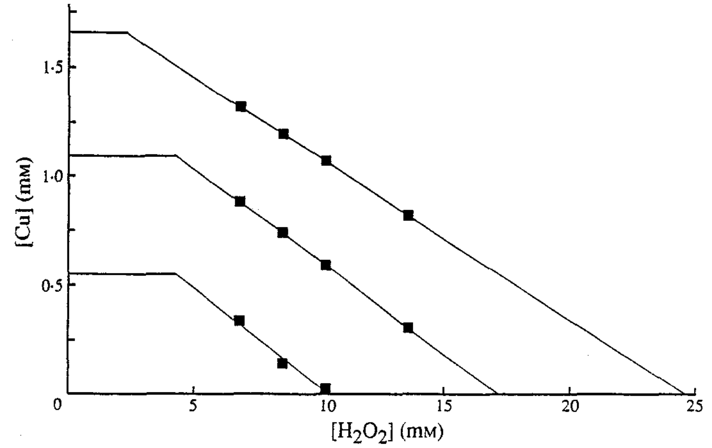

Fig. 4. Copper remaining in solution, in reaction solutions initially with 6·9 mM NaCN at pH 10·7, as a function of the peroxide concentration. The horizontal lines indicate the initial copper concentrations from top to bottom: 1·65, 1·10 and 0·55 mM $CuSO_4$.

Moreover, the concentration of peroxide required to begin precipitation of the copper, indicated by the projection of the plotted slopes to the initial copper concentrations, decreases as the copper concentration increases. This arises because more copper binds more cyanide to form $Cu(CN)_2^-$. With a fixed initial cyanide concentration, there is then less free cyanide to be oxidized as $Cu(CN)_3^{2-}$, which requires less peroxide before this initial stage of the reaction is completed.

The stoichiometry of the oxidation process which involves $Cu(CN)_2^-$ can be calculated from these data (Table 2). As the concentration of copper increases, the process becomes less efficient, with the ratio of peroxide consumed to $Cu(CN)_2^-$ rising to more than 6:1. This non-stoichiometric oxidation of $Cu(CN)_2^-$ is

Table 2. Stoichiometry of oxidation

Definition of subscripts: 0, initial; T, total; F, peroxide available at beginning of final stage, after free cyanide has been oxidized; C, peroxide consumed in oxidation of $Cu(CN)_2^-$

Concentrations	$[CN^-]_0$ (mM)	6·9	6·9	6·9
	$[Cu]_0$ (mM)	0·55	1·10	1·65
	$[Cu(CN)_2^-] = 2[Cu]_0$ (mM)	1·1	2·2	3·3
	$[CN^-] = [CN^-]_0 - 2\frac{1}{2}[Cu]_0$ (mM)	5·2	4·1	2·8
	$[H_2O_2]_T$ (mM)	10·2	17·3	24·6
	$[H_2O_2]_F = [H_2O_2]_T - [CN^-]$ (mM)	5·0	13·2	21·6
	$[H_2O_2]_C = [H_2O_2]_F - \frac{1}{2}[Cu]_0$ (mM)	4·7	12·6	20·8
Ratio	$[H_2O_2]_C/[Cu(CN)_2^-]$	4·3	5·7	6·3

undoubtedly the consequence of the copper-catalysed decomposition of H_2O_2. The copper(II)–peroxide system is complex and will not be elaborated here. In the present study the speciation of copper(II) is complicated by the presence of cyanide, cyanate, hydroxide, ammonia and carbonate.

Two observations, however, will be reported. The electronic absorption spectrum of the yellow solution which forms at the end of the first stage of the reaction displays, in addition to the band at 234 nm due to $Cu(CN)_2^-$, a broad absorption band around 360 nm. A yellow solution with a similar broad absorption around 360 nm can be obtained by mixing 1 mM $CuSO_4$ with 10 mM H_2O_2, in the absence of cyanide.

The second observation is that the appearance of the yellow colour at the end of the first stage of the reaction is accompanied by an abrupt increase in the hydroxide concentration over a few minutes; this is followed by a slow decrease over the hours during which time the copper precipitates.

Discussion

The oxidation of cyanide by peroxide is catalysed by copper in a three-stage process. The first stage is the reduction of Cu^{II} to Cu^{I} and the formation of $Cu(CN)_3^{2-}$. Oxidation then proceeds with the stoichiometry of 1:1 H_2O_2/CN^- until all of the excess cyanide is consumed, and the predominant copper species is $Cu(CN)_2^-$. With the millimolar concentrations employed this takes about an hour. At this point the reaction solution turns yellow. In the final stage further consumption of peroxide occurs until all of the cyanide has been oxidized and the copper is reoxidized to Cu^{II} and precipitates as $Cu(OH)_2$. In this stage the oxidation of cyanide is not efficient, with parallel decomposition of peroxide occurring. This non-productive consumption of peroxide increases with the amount of copper in the system. Hence the efficient oxidation of cyanide occurs with a high cyanide-to-copper ratio. This is achieved at the expense of the rate of the reaction, however, for the catalysed oxidation of the second stage is first order in the copper concentration.

The intermediates in the catalysed peroxide decomposition reactions have not been identified. Yellow-coloured species have been found in related systems: a brown complex was observed in the catalytic decomposition of peroxide by copper ammine complexes[9] and by copper hydroxide in the presence of citrate.[10] A dimeric copper(III) hydroxide complex has been identified as the yellow intermediate in the copper hydroxide-catalysed decomposition of hypochlorite and hypobromite.[11] Further investigation of the intermediates would require a better definition of the composition of the solutions than has been accomplished in the present work.

Acknowledgments

We thank John Cordner and Hank van Laar for bringing this problem to our attention and discussing some of their preliminary experiments with us.

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[9] Hayakawa, K., and Nakamura, S., *Bull. Chem. Soc. Jpn*, 1974, **47**, 1162.

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