



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201810945
Angew. Chem. 10.1002/ange.201810945

Link to VoR: <http://dx.doi.org/10.1002/anie.201810945>
<http://dx.doi.org/10.1002/ange.201810945>

Reversible hydrogen uptake/release over sodium phenoxide-cyclohexanol pair

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Dedication to 70th anniversary of Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Abstract: Hydrogen uptake and release in arene-cycloalkane pairs provide an attractive opportunity for on-board and off-board hydrogen storage. However, the efficiency of arene-cycloalkane pairs currently is limited because of unfavorable thermodynamics for hydrogen release. In this paper, we propose a strategy for optimizing the thermodynamics based on substitution of H in the -OH group of cyclohexanol and phenol with alkali or alkaline earth metals. The enthalpy changes of dehydrogenation decreases substantially, which correlates with the electron delocalized from oxygen to the benzene ring in phenoxides. Theoretical calculations reveal that replacement of H with a metal leads to a reduction in the energy gap of HOMO and LOMO and elongation of the C-H bond in the α site in cyclohexanol, which indicates the cyclohexanol is activated upon metal substitution. Our experimental results demonstrate that sodium phenoxide-cyclohexanol, an air and a water stable pair, can desorb hydrogen at ca. 413K and 373K in the solid form and in an aqueous solution, respectively. Hydrogenation, on the other hand, is accomplished at the temperatures as low as 303K.

The development of cost-effective, stable, and efficient energy carriers to store and transport energy, especially those generated from intermittent and distributed renewable resources, is vitally important. Hydrogen has long been viewed as an ideal energy carrier; however, storing hydrogen effectively is considered a grand challenge.^[1] Over the past two decades, significant research effort has focused on materials development for chemi- and physi-sorption of hydrogen.^[2] In particular, storing hydrogen in chemical bonds by the reduction of arenes offers the opportunity for using mass-produced chemicals,^[3] such as

toluene^[4] and dibenzene toluene,^[5] as hydrogen carriers to mediate the energy storage, transportation, and use chain. However, the technological implementation of those hydrocarbons suffers in part from low round trip storage efficiencies; that is, the large enthalpy change of dehydrogenation ($\Delta H_d = 60\text{-}70 \text{ kJ/mol-H}_2$)^[6] requires high temperatures to release hydrogen. Several strategies for circumventing or alleviating the thermodynamic constrain have been discussed in literatures, such as: I. non-thermal driven dehydrogenation via photocatalysis or electrocatalysis. Li et al. showed encouragingly that cyclohexane released H_2 at ambient temperature by using Pt/TiO_2 catalyst under visible light^[7]; dehydrogenation of N-heterocycles can also be realized at room temperature through photocatalysis or electrocatalysis.^[8] II. compositional alteration to optimize the thermodynamic properties of hydrocarbons. Previous efforts by Pez, Crabtree and Jessop in tuning the thermodynamics of dehydrogenation focused on incorporating heteroatoms, such as N, into the aromatic ring^[9] or substituting electron-donating groups for the aromatic ring.^[10] For example, ΔH_d and T_d , defined as the temperature at which the Gibbs free energy change for dehydrogenation at 1 bar hydrogen back pressure equals zero (i.e., $\Delta G_d = 0$) decrease from 73.6 kJ/mol- H_2 and ca. 599K for the cyclohexane-benzene pair to 67.3 kJ/mol- H_2 and ca. 546K for piperidine-pyridine pair, to ca. 65.6 kJ/mol- H_2 and ca. 532K for the cyclohexylamine-aniline pair.^[9b] Density functional theory (DFT) calculations also show that increasing the number of N atoms especially in the 1,3- or 1,3,5-arrangement of the ring or by incorporating a stronger electron-donating capability will reduce ΔH_d effectively.^[9b, 10] The ΔH_d can be manipulated by strengthening the aromatic character of the π systems to stabilize arenes and/or by weakening C-H or N-H bonding to destabilize the cycloalkanes (or hetero-cycloalkanes).

In this paper, we describe a new approach in materials development and thermodynamic alteration that involves introducing alkali and alkaline earth metal into the arene-cycloalkane pairs. The phenol-cyclohexanol pair (ΔH_d of ca. 64.5 kJ/mol- H_2 and T_d of 516 K^[11]) was chosen as the parent pair that subsequently was converted to alkali (or alkaline earth) phenoxide-cyclohexanol pairs. DFT calculations provide insight into the manipulation of the electronic properties and thermodynamics in hydrogen storage of the pairs. Experimental studies show three equivalents (equiv.) of hydrogen can be reversibly stored in the sodium phenoxide-cyclohexanol pair at 373K. To the best of our knowledge, this is the first report on the metallation of the cycloalkane-arene pair to achieve reversible hydrogen storage under moderate conditions.

The combined annual global production level of phenol and cyclohexanol is 1.1 billion tons. Cycling between phenol and cyclohexanol with a ~6 wt% or ~57 g/L reversible hydrogen capacity following R (1) provides an attractive route for hydrogen

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storage. Little attention, however, has been focused on this pair, possibly resulting from the unfavorable ΔH_d , (ca. 64.5 kJ/mol- H_2 corresponding to T_d of 516 K)^[11] and side reactions during dehydrogenation etc. On the other hand, the phenol/cyclohexanol pair has a distinct feature—the labile H of the OH group allows facile chemical modification. For example, phenol reacts with NaOH to yield sodium phenoxide and water as products of the acid-base reaction. We employed the Xls method^[12], which is based on DFT and neutral network, to simulate a number of alkali (or alkaline earth) phenoxides and cyclohexanolates and investigate the effect of replacing H of -OH with those basic elements. As shown in Figure 1a, the calculated dehydrogenation enthalpy change of cyclohexanol to phenol is 64.5 kJ/mol- H_2 is in good agreement with enthalpy change derived from known thermodynamic data,^[11] which validates the accuracy of the calculation method used in this study. Forming phenoxides by reacting phenol with metals (M=Li, Na, K, Mg and Ca) is thermodynamically favorable (Table S1). Analyses of the natural bond orbital charges show that electrons on O (Figure 1b and Table S2) of phenoxides are more delocalized resonating with the arene ring, thus forming p- π conjugation and consequently stabilizing the phenoxides. Formation of corresponding cyclohexanolates is also exothermic (Table S1), while a general observation is elongation of C-H bonding especially at the α site (Figure 1b and Table S3). As the magnitude of the conjugation effect is significantly greater than the hyper-conjugation effect of the same type, the exothermicity of phenol to phenoxide is greater than that of cyclohexanol to cyclohexanolate. The important consequence is the substantial decrease in ΔH_d of alkali (alkaline earth) cyclohexanolate-phenoxide pairs (Figure 1a). For example, dehydrogenation of sodium or potassium cyclohexanolate to corresponding phenoxide has ΔH_d values of 50.4 or 49.3 kJ/mol- H_2 , respectively, which are ca. 21.9% and 23.6% less than that of cyclohexanol to phenol. Alkali or alkaline earth metals donate more electrons than H on O, and the electrons delocalize through the p- π conjugation and stabilize. Therefore, we refer to the charge delocalized from O atom to the C-ring in phenoxides as an indication of the metallation effect (Table S2). A nonlinear relation between the ΔH_d and charge delocalized from the O atom to a C-ring in phenoxide was obtained (Figure 1a). The molecular structures of the Li, Mg, and Ca phenoxides are nearly of C2 symmetry, while Na and K cations bent over to the ring, which may cause charge redistribution within the system. It is worth mentioning that the lower ΔH_d calculated here is from a gas phase simulation. However, the ΔH_d in the solid phase may be even lower because of the π - π interaction among molecules in phenoxides, which stabilizes the phenoxides more than cyclohexanolates. We also note the findings of Jessop and co-workers^[10] in which the ΔH_d of cycloalkane scales with the Hammett parameter (σ) of substitute group, where the Hammett parameter is a measure of the electron-donating ability of the substituent group. Because the Hammett parameter of $-O^-$ (-0.81) is more negative than that of $-OH$ (-0.37)^[13], the substantial decrease in ΔH_d of alkali (alkaline earth) cyclohexanolate-phenoxide also is understandable from their viewpoint. Because different alkali or alkaline earth metals may lead to different $-O^-$ values, the ΔH_d reduction would vary depending on the metal involved.

Because the sodium cyclohexanolate-phenoxide pair is more appealing in terms of hydrogen density (4.9 wt%), ΔH_d (50.4 kJ/mol- H_2), and T_d (385 K) ($\Delta G_d=0$, assuming entropy change in dehydrogenation contributed mainly by hydrogen release) (see Figure 1a), we analyzed their electronic properties and compared the results with those of the parent cyclohexanol-phenol pair (see Figure 1c). Evidently, the replacement of H with Na redistributes the electron density. Compared to cyclohexanol, the energy level of highest occupied molecular orbital (HOMO) rises while lowest unoccupied molecular orbital (LUMO) drops, respectively, leading to a narrower HOMO-LUMO energy gap, which indicates sodium cyclohexanolate is easily activated.

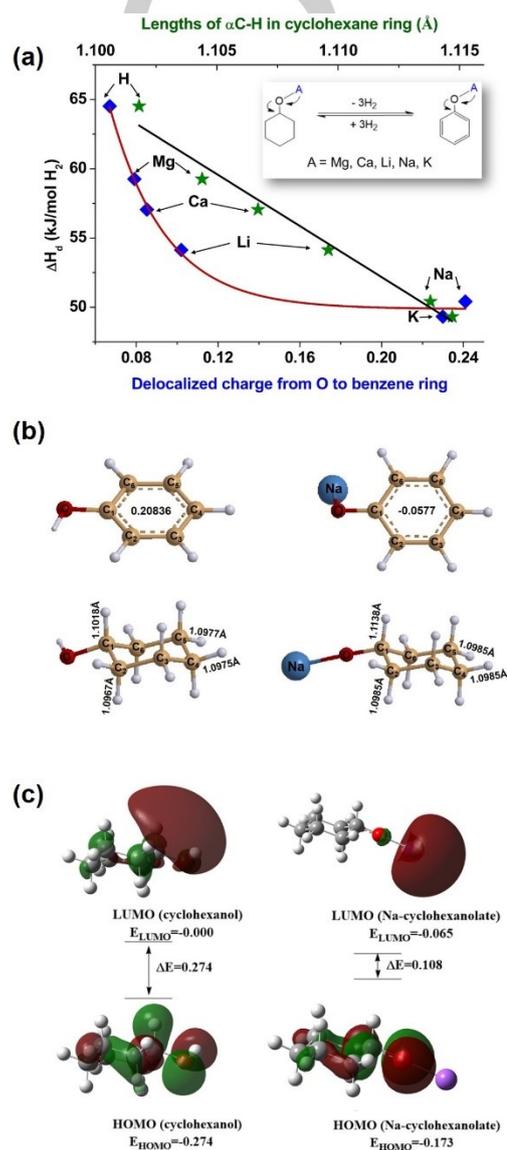
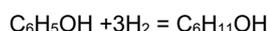


Figure 1. (a) Theoretical calculations on the ΔH_d in gaseous phase of metallated cyclohexanolates to phenoxides as a function of charge in the benzene ring and the length of C-H bond in α -site cyclohexanolate compared to that of cyclohexanol. The lines are guide to eye. (b) Charge in the benzene ring of phenoxide compared to that of phenol and the lengths of C-H bonds in cyclohexanolate compared to that of cyclohexanol. (c) The HOMO-LUMO energy gaps (a.u.) for cyclohexanol and sodium cyclohexanolate and the interfacial plots of the orbitals.



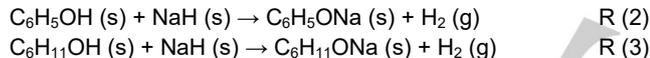
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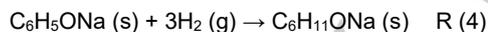
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This finding agrees well with the elongated α -C-H bond (Figure 1b and Table S3) where the first C-H bond dissociation is likely to occur. Because of the correlation of the kinetic barrier with the reaction heat (Brønsted–Evans–Polanyi relations), the increase in C-H bond length at the α site also scales with the dehydrogenation enthalpy change (Figure 1a and Table S4). With the substantial decrease in ΔH_d and promising kinetic feature, we synthesized sodium cyclohexanolate-phenoxide pair and evaluated its hydrogen uptake and release properties.

Sodium phenoxide and cyclohexanolate can be synthesized by mechanical ball milling phenol and cyclohexanol with NaH upon evolution of one equiv. hydrogen, respectively (details are given in experimental section and Supporting Information). We analyzed the products using X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) spectroscopy. The XRD pattern of synthesized sodium phenoxide matches well with that in the database (Figure 2a). The synthesized sodium cyclohexanolate, on the other hand, has poor crystallinity and presents a set of weak diffraction peaks at 7.6° , 16.8° , 21.3° , and 41.5° that cannot be assigned to any known material containing Na, C, O, and H. The ^1H NMR and FTIR spectroscopy measurements showed the absence of resonance of H of OH and -OH vibration from both cyclohexanolate and phenoxide (Figure 2b and Figure S1). On the other hand, the ^{13}C NMR spectrum of phenoxide, shows an obvious downshift compared with that of phenol, which is consistent with the increase in electron density in the C-ring determined from calculations (Figure S2). All these measurements suggest the formation of sodium phenoxide and sodium cyclohexanolate *via* reactions R (2) and R (3).



To confirm the thermodynamic data (ΔH_d) calculated from the XIs method,^[12] experiments were designed to measure the enthalpy change for hydrogenation of sodium phenoxide to cyclohexanolate using C80 Calvet calorimeter^[14]. The enthalpy change for the hydrogenation measured (R (4)) is approximately -156 kJ/mol (-52 kJ/mol-H_2), which agrees well with the calculated result (50.4 kJ/mol-H_2 for dehydrogenation). Details are given in Supporting Information.



Because of the decrease in ΔH_d , hydrogen release from the sodium phenoxide-cyclohexanolate pair would occur under moderate conditions. As cyclohexanolate and phenoxide are solid, both were ball milled with commercial catalysts (5% Ru/Al₂O₃ and 5% Pt/C) to assist the activation of hydrogen and the C-H bond during hydrogenation and dehydrogenation. As shown in Figure 3a, hydrogenation of sodium phenoxide under 30 bar hydrogen occurred slowly at ambient temperature in the presence of 5% Ru/Al₂O₃ catalyst, *ca.* 6 equiv. H were absorbed when the temperature was increased to 150°C where the product was characterized as sodium cyclohexanolate (Figure S9), showing full

hydrogenation. The hydrogenated sample then was dehydrogenated under vacuum. However, dehydrogenation proceeded very slowly at 150°C . We replaced the Ru/Al₂O₃ catalyst with 5%Pt/C catalyst and obtained appropriate dehydrogenation at temperatures above 100°C , about 5 equiv. H were desorbed at 140°C (Figure 3b), where the starting dehydrogenation temperature is around 90°C and sodium

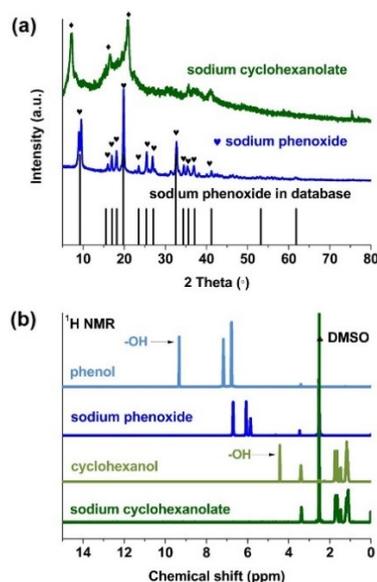


Figure 2. (a) X-ray diffraction patterns of synthesized sodium phenoxide and sodium cyclohexanolate. (b) ^1H NMR spectra of sodium phenoxide and sodium cyclohexanolate compared with that of phenol and cyclohexanol in DMSO.

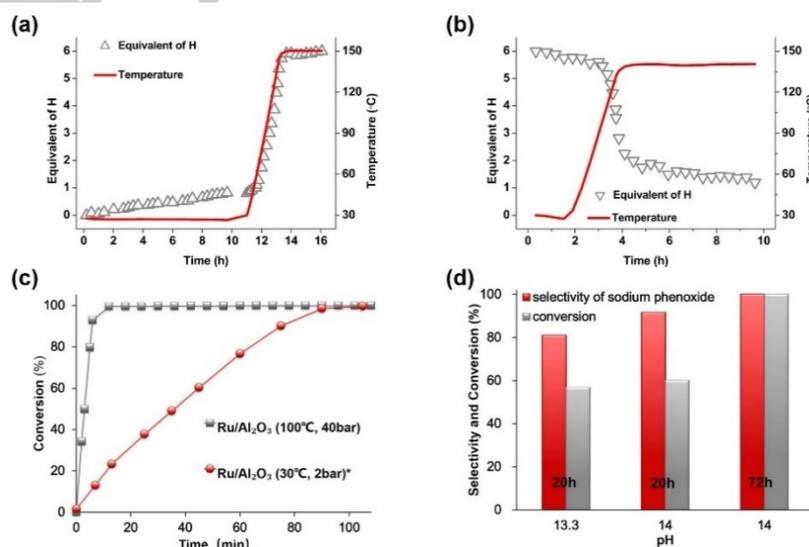
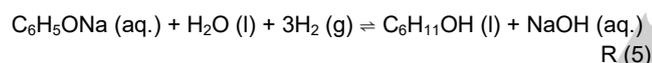


Figure 3. (a) Hydrogen uptake by sodium phenoxide catalyzed by 5%Ru/Al₂O₃ under 30 bar hydrogen. (b) Hydrogen release from sodium cyclohexanolate catalyzed by 5%Pt/C under vacuum. The molar ratios of metals to phenoxide (or cyclohexanolate) are 1:10. (c) Hydrogenation of sodium phenoxide in aqueous solution catalysed by 5%Ru/Al₂O₃ with the molar ratio of Ru to phenoxide of 1:30. *: $C_{\text{phenoxide}} = 0.148 \text{ mol/L}$, the molar ratio of Ru to phenoxide of 1:15. (d) Dehydrogenation of cyclohexanol in NaOH aqueous solution catalysed by 5%Pt/Al₂O₃ with different pH for 20 h or 72 h with the molar ratio of Pt to cyclohexanol of 1:50. Detail information can be found in Supporting Information.

phenoxide was obtained finally (Figure S10). Therefore, the metallation strategy proposed here successfully decreased the ΔH_d through forming phenoxide-cyclohexanolate pair, leading to lower T_d .

The slow kinetics in hydrogen uptake and release at lower temperatures shown in Figure 3a and 3b implies inefficient catalysis of solid Ru/Al₂O₃ or Pt/C on solid-state reactants. Therefore, we dissolved and dispensed the reactant and catalyst in water and re-investigated the properties of hydrogenation and dehydrogenation. It should be noted that sodium cyclohexanolate hydrolyzes into NaOH and cyclohexanol under the conditions applied in the experiment. Under these conditions, hydrogenation and dehydrogenation actually react via R (5), which has a ΔH_d of 182 kJ/mol (ca. 61 kJ/mol-H₂ obtained from C80 in the Supporting Information). Although with a higher ΔH_d , the entropy contribution of water may compensate such an enthalpy loss. As shown in Figure 3c, ca. 100% hydrogenation of sodium phenoxide can be achieved in 7.5 minutes at 100°C under 40 bar of hydrogen and in the presence of commercial 5%Ru/Al₂O₃ catalyst. Under a milder condition of 30°C and 2 bar hydrogen, hydrogenation of sodium phenoxide also can be achieved within 90 minutes. Cyclohexanol was detected by ¹H NMR (Figure S11). Previous studies also showed that the hydrogenation of hydrocarbons such as phenol^[15] and toluene^[16] can be facily carried out under mild conditions. However, dehydrogenation is usually kinetically problematic. Therefore, much attention is given to dehydrogenation.



Because cyclohexanol and NaOH are the hydrogenation products, we conducted the dehydrogenation of cyclohexanol and NaOH in aqueous solution catalyzed by commercial 5%Pt/C. Both phenoxide and cyclohexanone were found in the dehydrogenation products as shown in Figure 3(d) and Figure S12. Selectivity to phenoxide is pH dependent, i.e., the dehydrogenation of cyclohexanol in the presence of one equiv. of NaOH (pH = 13.3) has a conversion of cyclohexanol and selectivity to phenoxide of 56.9 % and 81.0 % after 20 hours reaction; with excess NaOH (pH = 14.0), both the conversion and selectivity reach 60.0 % and 91.7 % within the same periods of time. Prolonging the reaction leads to >99% conversion of cyclohexanol and selectivity to sodium phenoxide in aqueous phase. As H₂ is only detectable gaseous product, the yield of H₂ is > 99%. As hydrogen is the only detectable gaseous product (Figure S13), the reversed R (5) occurs at a temperature as low as 100°C. It is noteworthy that aqueous sodium phenoxide and cyclohexanol are stable in the air for weeks (Figure S14), which is a desirable property for hydrogen storage materials.

There are reports demonstrating that metallated (by alkali or alkaline earth metals) amidoboranes,^[17] hydrazinoboranes,^[18] and primary amines^[19] have reduced dehydrogenation temperatures and enhanced selectivity to hydrogen from their neat forms. In the present work, such a prominent effect of metallation also was achieved. The sodium modified cyclohexanol-phenol pair can undergo dehydrogenation at 100°C, which is substantially lower than the T_d for cycloalkanes (generally >300°C for thermal dehydrogenation)^[6] and for N-heterocycles and substituted cycloalkanes (generally >170°C for thermal dehydrogenation).^[10, 20] Although the dehydrogenation of 1,2,3,4-tetrahydroquinolines or indolines can be achieved at

relatively low temperature (refluxing of solvents such as toluene, xylene or 2,2,2-trifluoroethanol)^[21], only the N-containing rings were involved in the hydrogen release due to the delocalized π bond in the whole molecule after dehydrogenation. Furthermore, sodium phenoxide can be prepared by reacting phenol and NaOH; therefore, it can be mass produced at low cost. It is stable in air and water and has a low vapour pressure. All these characteristics make the sodium phenoxide-cyclohexanolate pair a very attractive hydrogen storage material for practical applications. Further efforts should focus on materials engineering including developing more efficient hydrogenation/dehydrogenation catalyst and reaction medium.

Acknowledgements

T.H. and P.C. acknowledge the supports provided by the National Natural Science Foundation of China (21875246, 51671178, 51472237), DICP (DICP ZZBS201616), Sino-Japanese Research Cooperative Program of the Ministry of Science and Technology (2016YFE0118300) and iChEM-2011. A.W. would like to acknowledge the financial support provided by the National Science Foundation of China (NSFC) (21773193) and the fundamental research Funds for the Central Universities (20720160031). T.A. and A.K. gratefully acknowledge support from the Hydrogen Materials – Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office. Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Keywords: reversible hydrogen storage • metallation • organic hydride • thermodynamic modification

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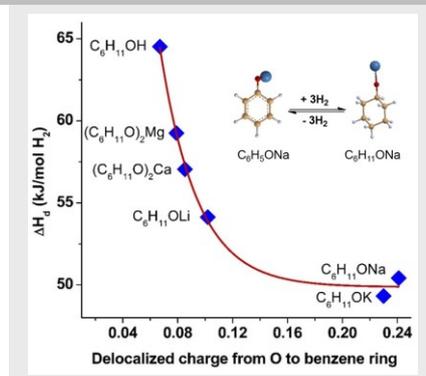
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