Thermal behaviour of some rhodium(II) cycloalkanocarboxylate complexes

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Abstract

Thermal properties of cycloalkanecarboxylates $[Rh_2(O_2CR)_4]$ (R = C_3H_5, C_4H_7, C_5H_9 and C_6H_{11}) were studied and the results compared with those obtained for $[Rh_2(O_2CR)_4]$ (R = CH_3, C_2H_5 and C_3H_7). Thermogravimetry and differential scanning calorimetry were used as the techniques and the heats of reaction for the samples in open and closed crucibles were obtained, in different atmospheres. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal decomposition of metal carboxylates has been for a long time the subject of numerous investigations, chiefly in view of the preparation of metal and metal oxide catalysts [1,2]. In this sense, rhodium carboxylates are specially interesting because of the high catalytic activity conferred to rhodium and their metal oxides. Kitchens and Bear [3–5] have discussed the behaviour of some of these compounds (acetate, propionate and butyrate) in a series of reports and have found that on heating to 400°C such complexes decompose to metallic rhodium. The thermogravimetric studies were carried out in nitrogen atmosphere and the authors mention that no oxide is formed even if the decomposition is performed in air.

Our investigation is concerned with the study of the thermal properties of rhodium(II) cycloalkanecarboxylates by thermogravimetry and differential scanning calorimetry. Of particular interest were the variation of the heats of reaction for open and closed crucibles, cage breakdown and analysis of the thermodecomposed residue in different atmospheres.

2. Experimental

Preparation of the complexes: Rhodium(II) carboxylates were prepared by the method previously described in the literature [5,6].

Elemental analysis: Calculated for $[Rh_2(O_2CC_3H_5)_4]$: C, 35.19; H, 3.69. Found: C, 35.53; H, 3.63. Calcd for $[Rh_2(O_2CC_4H_7)_4]$: C, 39.89; H, 4.69. Found: C, 39.80; H, 4.67. Calcd for $[Rh_2(O_2CC_5H_9)_4]$: C, 43.79; H, 5.51. Found: C, 43.42; H, 5.52. Calcd for $[Rh_2(O_2CC_6H_{11})_4]$: C, 47.07; H, 6.21. Found: C, 47.12; H, 6.21.

Magnetic measurements: Magnetic measurements were carried out by the Faraday method in a CAHN

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system model DTL 7500 using $Hg[Co(SCN)_4]$ as the calibrant.

Infrared spectra: The IR spectra were obtained using KBr discs (4000–500 cm^{-1} range) on a Bomem spectrophotometer model BM 102.

Thermal studies: Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded with a Perkin-Elmer TGA7 system employing a heating rate of 5 K min^{-1}, dynamic air or nitrogen atmosphere (ca. 30 ml min^{-1}) and sample masses in the range of 2–5 mg. Differential scanning calorimetry (DSC) curves were recorded on Cells DSC25 of to Mettler System TA 4000 employing a heating rate of 5 K min^{-1}, sample masses between 1 and 2 mg in open and in closed aluminum crucibles. All samples were heated in dynamic air and nitrogen atmosphere (ca. 30 ml min^{-1}). For ΔH measurements, the DSC system was calibrated with indium (m.p. 156.6°C; $\Delta_{fus}H = 28.54$ J g^{-1}). The analyses of the gaseous products were carried out using the flow apparatus shown in Fig. 1. A reaction vessel (a), was mounted in the furnace horizontally (b) and connected to a series of traps. The trap (c) was cooled in dry ice to condense the low boiling point product, while the solutions of the other two traps (d) reacted with the high boiling point gases evolved. In the trap (d.1) barium hydroxide solution was used for identification of CO_2, while in the other trap (d.2) was palladium(II) chloride solution placed for identification of CO. The sample (ca. 50 mg) was introduced on

the porcelain crucible and the apparatus swept out with nitrogen for half an hour at a flow rate similar to that used in the thermal decomposition experiments (30 ml min^{-1}). The furnace temperature was raised at ca. 10 K min^{-1} to a final temperature of ca. 400°C.

Residue analysis: Analyses of the liquid samples were performed by ^1H and ^{13}C NMR and gas chromatography coupled with mass spectrometry. The apparatus used for gas chromatography was a VARIAN model (capillary column 30 m, obtained in the range 30–70°C at rate 5 K min^{-1}). NMR spectra were obtained using a 200 MHz BRUKER with the sample in chloroform-d solution. The solid samples were analyzed by powder X-ray diffraction methods. The apparatus used for X-ray diffraction was an IRIS diffractometer model 6.

3. Results and discussion

The fact that the compounds have been isolated as powders and not as single crystals from the aqueous solution means that a complete structure determination cannot be determined. However, the magnetic and IR data (Tables 1 and 2, respectively) enable us to predict that the compounds have similar structures to the previously studied rhodium carboxylates (for example, acetate and propionate) [5]. The compounds $[Rh_2(O_2CC_3H_5)_4]$, $[Rh_2(O_2CC_4H_7)_4]$, $[Rh_2(O_2CC_5H_9)_4]$ and $[Rh_2(O_2CC_6H_{11})_4]$ present a Rh–Rh bond with a decrease of the magnetic moment, expected for the isolated metal ions due to the spin pairing of two Rh(II) centers. Moreover, in accordance with Deacon's works [7], the IR spectroscopic studies suggest that the carboxylate groups have a bidentate co-ordi-
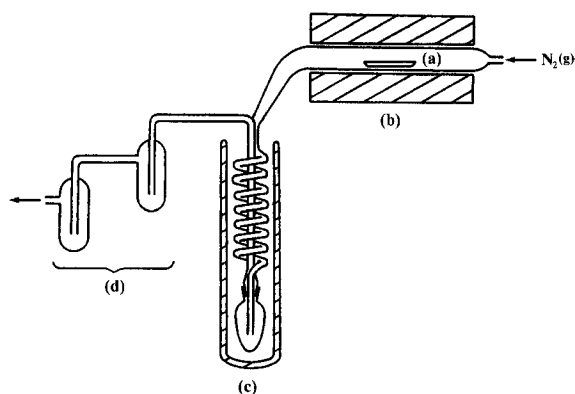

Fig. 1. Evolved gas collecting system of the thermal analysis (absorbed/condensed system): (a) reaction vessel; (b) furnace; (c) trap for condensation; (d) trap for identification reactions.

Table 1
Magnetic susceptibility of the rhodium(II) alkanocarboxylates at 20°C

Compounds	$\chi_M \times 10^4$ (cgs units mol^{-1})[a]	μ_{eff} (M.B.)[b]
$[Rh_2(O_2CC_3H_5)_4]$	1.16	0.52
$[Rh_2(O_2CC_4H_7)_4]$	1.98	0.69
$[Rh_2(O_2CC_5H_9)_4]$	3.07	0.85
$[Rh_2(O_2CC_6H_{11})_4]$	1.88	0.67

[a] χ_M is the molar susceptibility.
[b] μ_{eff} is the effective magnetic moment.

Table 2
Maximum temperature and ΔH of thermal decomposition reaction of the rhodium(II) cycloalkanocarboxylate complexes

Compounds	Open crucible				Closed crucible	
	N_2		Air		N_2	
	T (°C)	ΔH (kJ mol^{-1})	T (°C)	ΔH (kJ mol^{-1})	T (°C)	ΔH (kJ mol^{-1})
[Rh$_2$(O$_2$CC$_3$H$_5$)$_4$]	288.2	−1404.9	298.2	−2547.3	255.3	194.0
[Rh$_2$(O$_2$CC$_4$H$_7$)$_4$]	281.6	−1360.2	272.6	−2069.9	277.0	220.3
[Rh$_2$(O$_2$CC$_5$H$_9$)$_4$]	290.2	−1647.8	280.8	−2410.2	295.8	335.2
[Rh$_2$(O$_2$CC$_6$H$_{11}$)$_4$]	296.7	−1687.9	292.4	−2420.2	312.7	4.2

nation bridging to two rhodium atoms and conferring a binuclear structure in the form of a cage.

3.1. Thermal analysis

3.1.1. Thermogravimetry

TG and DTG curves under dynamic nitrogen atmosphere for the four complexes, [Rh$_2$(O$_2$CR)$_4$] (R = C$_3$H$_5$, C$_4$H$_7$, C$_5$H$_9$ and C$_6$H$_{11}$) are given in Fig. 2. As can be seen, for all complexes the thermal

decomposition process occurs abruptly in a single step, with DTG maxima at 290°C, 255°C, 288°C and 265°C, respectively.

The TG curves for rhodium(II) cyclopropane, cyclopentane and cyclohexane carboxylate show three thermal events between 25°C and 925°C. The first thermal event observed between 250°C and 300°C, accompanied by a mass loss (62%, 67% and 70%, respectively) equivalent to four molecules of ligand (expected mass loss 62.2%, 68.7%, 71.2%,
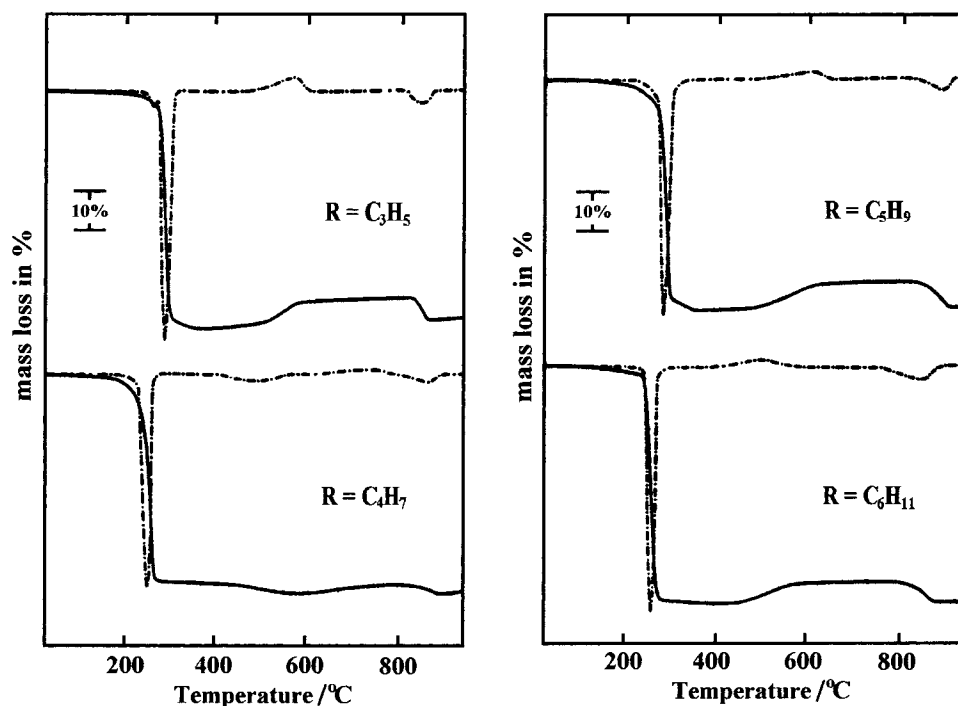

Fig. 2. TG and DTG curves of the [Rh$_2$(O$_2$CR)$_4$] (R = C$_3$H$_5$, C$_4$H$_7$, C$_5$H$_9$, C$_7$H$_{11}$) in dynamic N$_2$ atmosphere (ca. 30 ml min^{-1}) at a heating rate of 5 K min^{-1}.

respectively) suggests the formation of Rh metal (dark brown colour). In the range 500–700°C the TG curves display a gradual mass gain of about 8%, suggesting that Rh_2O_3 is the eventual solid product. Under nitrogen atmosphere, and at temperatures higher than 900°C, Rh_2O_3 decomposes again to Rh metal (silvery-gray colour). This difference in Rh metal residue colour obtained at different temperatures can be assigned to an unequal crystal assembly.

For rhodium cyclobutanecarboxylate the TG curve displays four thermal events between 25°C and 925°C. The first thermal event was observed between 250°C and 300°C accompanied by a 60% mass loss. The residue from decomposition has no clearly defined composition. At higher temperatures (550–600°C), a second gradual mass loss of about 4–5% is observed. The total mass loss was found to be 65%, suggesting that Rh metal is the final solid product of the decomposition. This is followed by the third step which starts at 620°C and is accompanied by a 4–5% mass gain. The fourth and last step starts at 875°C and is again accompanied by a 4–5% mass loss.

Similar results were obtained in dynamic air atmosphere, although higher initial (T_i) and final (T_f) decomposition temperature are usually observed. Moreover, a rich oxygen atmosphere facilitates oxidation of the intermediary residue to an oxidized form and conserves its stochiometry above 900°C.

3.1.2. Differential scanning calorimetry

Differential scanning calorimetry for compounds was performed in open and closed crucibles in two different atmosphere (N_2 and air). Figs. 3 and 4 show DSC curves under nitrogen atmosphere. Table 2 presents the temperature peaks and the heats of reaction (ΔH).

As can be seen, the DSC curves profile was very similar for all complexes. The results in closed crucibles (not hermetically) resemble those described in [10], with two marked thermal event regions (Fig. 3). The region between 255°C and 315°C reveals at least two overlapping endothermic peaks, except for rhodium cyclopentane carboxylate which shows only one peak, assigned to the cage breakdown. This observation indicates that the event referring to the ligand loss is apparently complex. The second region above 400°C is marked by broad, weak and endothermic
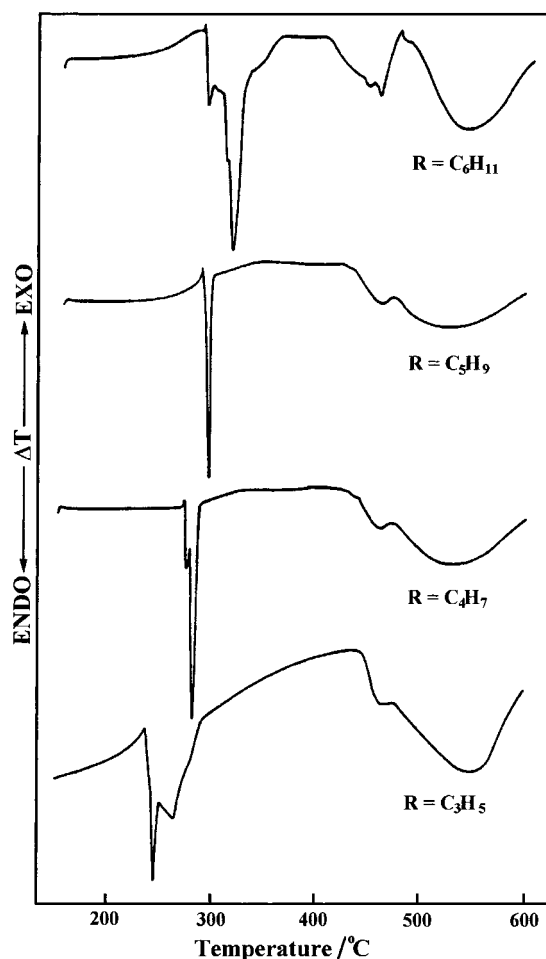

Fig. 3. DSC curves in closed crucible of the $[Rh_2(O_2CR)_4]$ (R = C_3H_5, C_4H_7, C_5H_9, C_7H_{11}) in dynamic N_2 atmosphere (ca. 30 ml min^{-1}) at a heating rate of 5 K min^{-1}.

peaks which are associated with a gradual mass gain process.

However, the resulting DSC curves in open crucibles were essentially different with two marked thermal event regions (Fig. 4). In the first region at 250–300°C one intense sharp exothermic peak is observed (Table 2). In this case, the event is exothermic because there is no block to the release of gas. Kinetic decomposition studies of rhodium(II) acetate have shown that in the cage breakdown, initial formation of RhO_2 occurs followed by formation of a Rh product [11]. The author reported that in these stages the process is strongly accelerated at these temperatures.
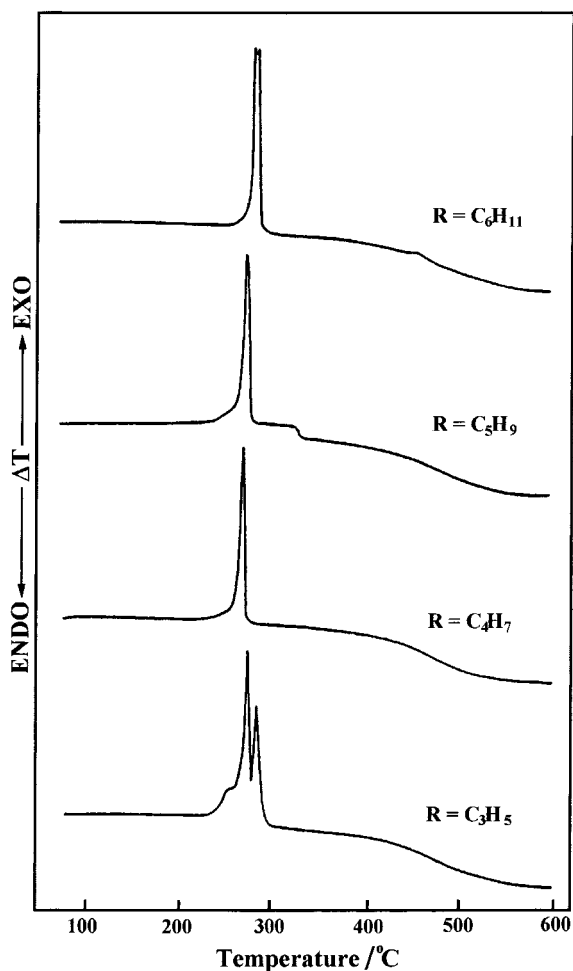
Fig. 4. DSC curves in open crucible of the $[Rh_2(O_2CR)_4]$ ($R = C_3H_5$, C_4H_7, C_5H_9, C_7H_{11}) in dynamic N_2 atmosphere (ca. 30 ml min^{-1}) at a heating rate of 5 K min^{-1}.

3.2. Product analysis

3.2.1. Solid phase products

The solid residues obtained for all compounds at different temperatures in N_2 were analyzed by X-ray diffraction (Figs. 5 and 6). The main lines are shown in Table 3. Figs. 5 and 6 show X-ray diffractograms of isolated residues at several temperatures for two representative complexes.

Contrary to rhodium cyclobutanecarboxylate, the X-ray results showed that the material obtained at the intermediate temperature of 450°C is amorphous (Fig. 5). However, in the range of 700–800°C and 900–925°C more crystalline materials have been obtained, whose powder patterns of the residue agree with those of Rh_2O_3 and Rh metal, respectively [8]. Moreover, the infrared spectrum of the residue obtained in the range 700–800°C shows bands at 655(s), 548(m), 500(w) cm^{-1} that can be assigned to rhodium–oxygen stretching frequencies [9]. At temperatures higher than 900°C, the X-ray pattern of the residue obtained indicates the presence of metallic rhodium (Table 3).

For rhodium cyclobutanecarboxylate the results of X-ray diffraction (Fig. 6) showed that the residue obtained in the range 250–300°C has some reflection of Rh metal, although with low crystallinity. The products in the range 550–600°C show an X-ray pattern of an amorphous solid, but at higher temperatures, in the range 650–700°C the resulting residue exhibits certain crystallinity with the principal lines indicated in Table 3. In this temperature range, the TG curves indicate a mass gain corresponding to RhO stoichiometry, but such material is still unknown. Above 900°C, the X-ray pattern of the residue obtained indicates the presence of Rh metal (Table 3).

3.2.2. Gas phase products

The high boiling point products collected in trap (c) were submitted to mass spectrometry and ^1H and ^{13}C NMR analysis. The results showed that one of the products formed in the thermal decomposition of the rhodium(II) cycloalkanocarboxylates corresponds to a carboxylic acid.

Table 3
Relative intensities and interplanar distances obtained from X-ray diffractograms of Rh, RhO(?) and Rh_2O_3 residue

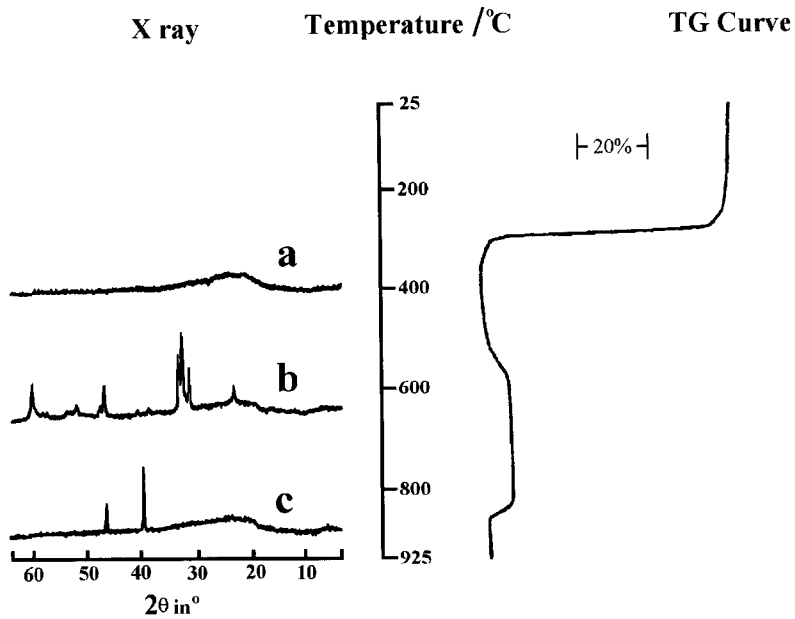| Residue	d (Å) (I/I_0)
Rh	2.20 (100), 1.90 (50)
RhO(?)	2.61 (100), 2.86 (61), 2.31 (42), 3.00 (38), 1.70 (24), 2.19 (21)
Rh_2O_3	2.62 (100), 2.57 (71), 2.72 (57), 1.50 (40), 1.87 (39), 3.68 (27), 1.70 (15), 1.84 (13)

Fig. 5. TG curves and X-ray diffractogrames for the thermal decomposition residue of rhodium(II) cyclopropanecarboxylate. Obtained residue in the range: (a) 350–450°C; (b) 700–800°C; (c) above 900°C.
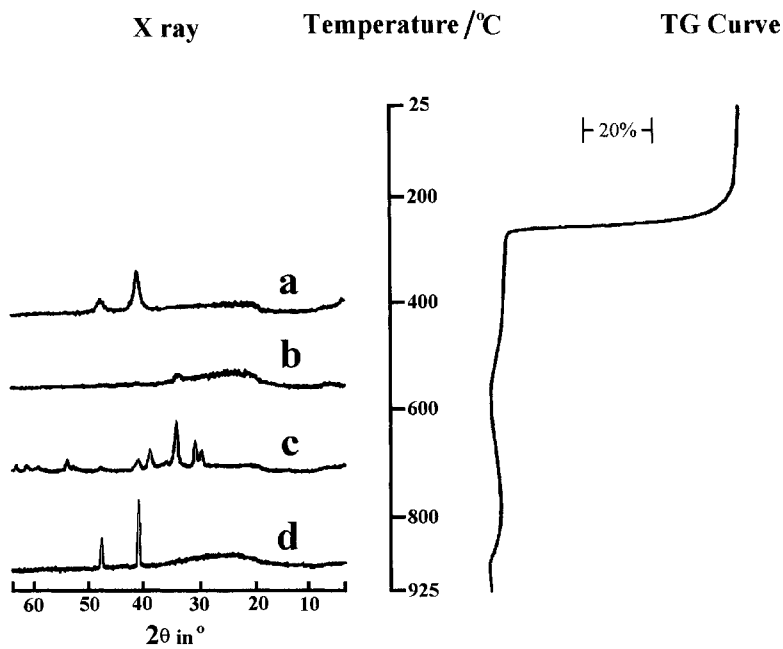

Fig. 6. TG curves and X-ray diffractogrames for the thermal decomposition residue of rhodium(II) cyclobutanecarboxylate. Obtained residue in the range: (a) 300–400°C; (b) 500–550°C; (c) 700–800°C; (d) above 900°C.

When low boiling point gases are bubbled through an aqueous solution of $Ba(OH)_2$ (trap (d), Fig. 1) we observe that no reaction occurs, while in the palladium chloride solution reduction to palladium occurs, meaning that during thermal decomposition reducing gases are liberated. Despite the fact that we have not identified the substance, it has been shown in the literature the liberation of carbon monoxide during the thermal decomposition of rhodium acetate [4]. We believe that the same event may happen with our compounds.

Acknowledgements

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