Hydrogenation of aqueous mixtures of calcium carbonate and carbon dioxide using a water-soluble rhodium(I)–tertiary phosphine complex catalyst

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Dedicated to Professor Józef J. Ziółkowski on the occasion of his 70th birthday in recognition of his outstanding contributions to organometallic chemistry and catalysis.

Abstract

Aqueous suspensions of calcium carbonate were hydrogenated to yield calcium formate under a gas phase containing both H_2 and CO_2. A rhodium(I)-complex of monosulfonated triphenylphosphine (mtppms), $[RhCl(mtppms)_3]$ was used as catalyst. Reaction temperatures were in the range of 20–70 °C, total pressure 10–100 bar with an optimum $p(CO_2):p(H_2)$ ratio of 1:4. Due to the mobile bicarbonate-formate equilibrium, the highest available formate concentration is decreased with increasing temperature but increased with increasing pressure. Interestingly, at 50 °C and 100 bar total pressure the yield of formate was 143% (based on $CaCO_3$) which implies the formation of free formic acid in the reaction of CO_2 from the gas phase. The dependence of the hydrogenation rate on the catalyst and ligand concentrations, as well as that of the decomposition of formate as a function of temperature were also studied.
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1. Introduction

Homogeneous catalytic conversion of carbon dioxide into useful products has attracted much recent interest [1–8]. Carbon dioxide is cheap and easily available not only highly diluted in the atmosphere but in high concentrations, too, at natural or industrial sources (fossil-carbon fuelled generator plants, beer factories, etc.). In the last few years, important advances have been made in the homogeneous catalytic hydrogenation of carbon dioxide under supercritical or near-critical conditions [9–11], in coupling of CO_2 and epoxides yielding polycarbonates [3] and in the practical synthesis of 2-ethylheptanoic acid from carbon dioxide, butadiene and hydrogen [12].

Perhaps the largest volume process on Earth is the fixation of CO_2 as carbohydrates during the green plant photosynthesis – these reactions take place in a bulk aqueous environment. It is also noteworthy that the CO_2 content of industrial gases is removed by washing with aqueous solutions of bases particularly of amines or amino-alcohols. This has generated active research into the use of aqueous solutions for the hydrogenation of carbon dioxide with water-soluble catalysts [7,13]. In the first successful hydrogenation of CO_2 in a fully aqueous system the K[RuCl(edta-H)] catalyst (edta-H = monoprotonated ethylenediaminetetraacetate trianion) converted CO_2 with a turnover frequency (TOF) of 375 h^{-1} under mild conditions [14] (TOF = mol product/mol catalyst × time). Importantly, this reaction did not require the addition of bases. Later it was found that several water-soluble Rh(I)- and Ru(II)-complexes, in many cases with hydrophilic tertiary phosphine ligands, were

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able to catalyze the hydrogenation of CO_2 in aqueous systems in the presence of organic amines or amino-alcohols yielding the corresponding ammonium formates or formamides with TOFs up to several thousand [15]. For example, in aqueous $HNMe_2$ solutions with $H_2:CO_2 = 1:1$, $p = 40$ bar and $T = 81\,^{\circ}C$ the water-soluble $[RhCl(mtppts)_3]$ (mtppts $= 3,3',3''$-phosphinetriylbenzenesulfonic acid, *m*-trisulfonated triphenylphosphine, usually as sodium salt) catalyst afforded dimethylammonium formate with an initial TOF of $7260\,h^{-1}$ [15]. However, in the absence of $HNMe_2$ or other nitrogen bases this catalyst was completely inactive for the hydrogenation of CO_2. Several other rhodium complexes are also known to catalyze the hydrogenation of carbon dioxide in partially or fully aqueous solutions [16–19]. In all cases the addition of either an amine or an alcohol was found essential to achieve reasonable rates and total conversions. It was also established, that the nitrogen bases not only facilitated the reaction through their reaction with the product formic acid but played an active role also in the formation of the catalytically active monohydridorhodium(I) species such as e.g. $[RhH(S)(mtppts)_3]$ (S = solvent or amine) [15]. An important feature of the reactions run in the presence of amines is that the final concentration of the product formic acid (formate, formamide) never exceeded that of the amine. This is in contrast to the case of dipolar aprotic solvents (e.g. dmso) when with certain amines HCOOH/amine > 1 could be observed (for example with NEt_3 this ratio was 1.6) [20].

The last few years saw extensive studies on the homogeneous hydrogenation of bicarbonates (Eq. (1)) or carbonates in aqueous solutions. The catalysts used included $[RuCl_2(pta)_4]$ (pta = 1,3,5-triaza-7-phosphaadamantane) [21], $[\{RuCl_2(mtppms)_2\}_2]$ (mtppms = (3-diphenylphosphino)benzenesulfonic acid, *m*-monosulfonated triphenylphosphine, sodium salt) [22], $[RuCl_3(NO)(PR_3)_2]$ ($PR_3 =$ mtppms or mtppts) [23], and the $[(\eta^6\text{-arene})RuH(PR_3)_2]^+$ complexes formed under hydrogen from $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ and PR_3 (arene = benzene or *p*-cymene, $PR_3 =$ mtppms or mtppts or pta) [24]. To a lesser extent, $[RhCl(mtppms)_3]$ has also been studied as catalyst for reaction (1) [25].

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \qquad (1)$$
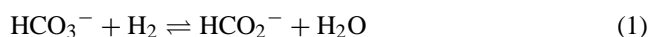
These reactions did not require the addition of an organic base, however, with the above catalysts hardly any hydrogenation of aqueous CO_2 solutions (carbonic acid) could be observed. In contrast, $NaHCO_3$ was hydrogenated to $NaHCO_2$ at 20–80$\,^{\circ}C$ and $p(H_2) = 1$–100 bar with TOFs up to $9600\,h^{-1}$ [22] with nearly quantitative yields.

Based on our experience in the homogeneous hydrogenation of bicarbonates, it seemed reasonable to us to explore the possibility of the hydrogenation of alkaline earth metal carbonates, specifically $CaCO_3$ in aqueous suspensions under a CO_2 atmosphere. On the action of CO_2 and H_2O (carbonic acid) $CaCO_3$ dissolves and takes part in several equilibria in solution, depending mostly on the pH [26]. At low CO_2 pressures in the absence of added acids or bases the composition of the solution can be regarded as that of a solution of the hypothetical $Ca(HCO_3)_2$, however, at lower pH (higher CO_2 pressures) the molar ratio of the $Ca(HCO_3)^+$ ion pair becomes significant [26] leaving less free bicarbonate available for hydrogenation. Since the dissolution requires aqueous solvents, water-soluble catalysts [13] are uniquely suited for this reaction. Calcium formate is a valuable product used in leather tanning and in the production of silage in animal nutrition [27]. In addition, cheap $CaCO_3$ is available in huge quantities and its use may contribute to the utilization of CO_2 by affordable means.

Here we present in detail our findings on the hydrogenation of aqueous suspensions of $CaCO_3$ under CO_2 pressure using $[RhCl(mtppms)_3]$ as catalyst. The effects of the variation of experimental conditions are also reported and allow some insight into the kinetic details of the reaction. An earlier communication of us has already disclosed the suitability of this Rh-complex as catalyst for this purpose [28].

2. Experimental

2.1. Materials and analytical techniques

mtppms and $[RhCl(mtppms)_3]$ were prepared according to published procedures [29] and checked by ^1H, ^{31}P NMR and IR spectroscopy. H_2, CO_2 and Ar were obtained from Linde. Analytically pure $CaCO_3$ was supplied by Reanal, Hungary. Other materials were highest purity commercial products of Aldrich and Merck and were used as received. Doubly distilled water was used throughout.

^1H and ^{31}P NMR spectra were recorded on a Bruker DRX400 equipment in D_2O. Infrared spectra were recorded on a PE Paragon 1000 PC FT-IR spectrometer in KBr discs. The reaction mixtures were analyzed for formate (as formic acid) by HPLC (Waters 501 pump, Supelcogel$^{\circledR}$ 610H column thermostated to 30$\,^{\circ}C$, Waters 490E multiwavelength UV–vis detector at $\lambda = 210$, 205 and 254 nm, sample volume 10 μL, eluent 0.1% H_3PO_4 in water, flow rate 1 mL min^{-1}).

2.2. Hydrogenation experiments

These experiments were run either in home-made heavy-walled glass reactors (total volume 150 mL) up to ≤ 10 bar total pressure or in glass-lined stainless steel reactors (up to ≤ 100 bar) both equipped with a gas inlet, pressure gauge and an inlet/sampling port. In a typical run 100 mg (1 mmol) $CaCO_3$, 13.4 mg (1×10^{-5} mol Rh) $[RhCl(mtppms)_3]$, 6.0 mg (1.5×10^{-5} mol) mtppms and a Teflon covered stir bar were placed into the reactor. After closing the reactor it was deoxygenated with several evacuation/refill (Ar) cycles. Then 10 mL of water was injected through the inlet port. The reactor was evacuated and filled first with CO_2 followed by H_2 of the desired pressure at room temperature, then placed into an oil bath of the desired tem-

perature which was controlled by a Lauda K4R circulator (glass reactor) or wrapped around with a heating mantle connected to a toroid transformer (stainless steel reactors). The reaction mixture was vigorously stirred using a magnetic stirrer. At the end of the desired reaction time the reactor was cooled in ice water, the pressure vented carefully and the formate content of the product mixture was determined by HPLC (vide supra).

3. Results and discussion

When a fine powder of calcium carbonate was stirred in water in the presence of [RhCl(mtppms)$_3$] under an atmosphere containing both CO_2 and H_2 a clean hydrogenation occurred yielding formate as the sole product (Eq. (2), Fig. 1). This successful attempt to hydrogenate $CaCO_3$ in a homogeneously catalyzed reaction under mild conditions is made possible by the combination of acid–base chemistry in water and aqueous organometallic catalysis.

$$CO_3^{2-} + CO_2 + 2H_2 \rightleftharpoons 2HCO_2^- + H_2O \qquad (2)$$

The reaction is rather slow and under the conditions of Fig. 1 the concentration of HCO_2^- levels off in time much below the stoichiometric value (200 mM) based on Eq. (2). Earlier attempts of $CaCO_3$ hydrogenation are sporadic and the heterogeneous catalytic processes described in the literature [30] require harsh conditions. In general $CaCO_3$ has to be decomposed to yield CO_2 which becomes subsequently hydrogenated. There are also observations on that when Pd or Ir metal is deposited on calcium carbonate the surface layer of the support is able to react with spilt-over hydrogen to yield CH_4 already at 300 °C, well below the decomposition temperature of $CaCO_3$. Nevertheless, this temperature is still much higher than those applied in this study.

It is also seen in Fig. 1 that at the beginning of the reaction the concentration of $[HCO_2^-]$ increases linearly in time and therefore in the following discussion the formate concentra-
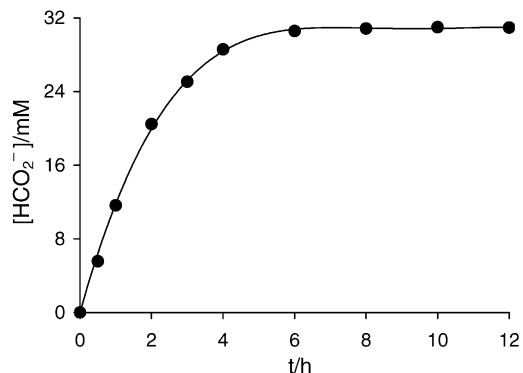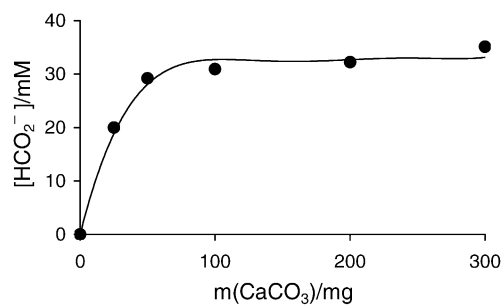
Fig. 2. Effect of the amount of $CaCO_3$ on the rate of the hydrogenation of $CaCO_3/CO_2$ catalyzed by [RhCl(mtppms)$_3$] in aqueous suspension/solution. [Rh] = 1 mM, [mtppms]$_{total}$ = 4.5 mM, $p(CO_2)$ = 2 bar, $p(H_2)$ = 8 bar, T = 60 °C, V = 10 mL, t = 15 h.

tion obtained in 1 h reactions is used for the characterization of the initial reaction rate.

The activity of the catalyst is influenced by the concentration of the phosphine ligand. An optimum value is obtained by the addition of 1.5 mol mtppms to [RhCl(mtppms)$_3$] ([mtppms]$_{total}$/[Rh] = 4.5). Increasing the concentration of the catalyst increases the rate almost linearly up to [Rh] ≤ 2 mM, however, at higher concentrations the rate of the reaction tends to level off. This latter behaviour is the consequence of the bicarbonate/formate equilibrium (vide infra). In most of the experiments discussed here we used 10 bar total pressure; a maximum in the reaction rate as a function of the gas phase composition was found at $p(CO_2):p(H_2)$ = 1:4, i.e. at $p(CO_2)$ = 2 bar and $p(H_2)$ = 8 bar. (The effects of the above parameters are shown as supplementary information, Supplementary Figures 1–3.) The amount of formate obtained in the first hour of the hydrogenations initially shows a rapid increase as a function of the amount of solid $CaCO_3$ in the suspension (Fig. 2), however it soon reaches a limiting value and a further increase of the amount of $CaCO_3$ leads only to negligible improvement of the formate yield.

The effect of the temperature on the reaction is twofold. As can be seen in Fig. 3, the initial rate increases exponentially with increasing temperature and the Arrhenius plot of the data leads to an apparent activation energy of 36 kJ mol^{-1}. This value is close to those obtained in the hy-
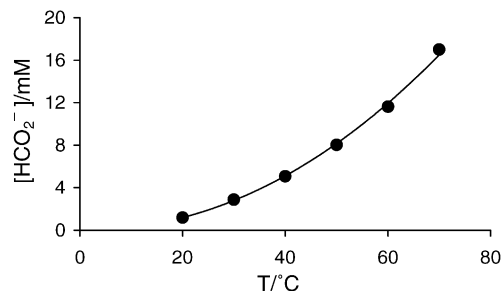
Fig. 1. Time course of the hydrogenation of calcium carbonate in aqueous suspension under CO_2 pressure catalyzed by [RhCl(mtppms)$_3$] in the presence of added mtppms. m($CaCO_3$) = 100 mg (1 mmol), [Rh] = 1 mM, [mtppms]$_{total}$ = 4.5 mM, $p(CO_2)$ = 2 bar, $p(H_2)$ = 8 bar, T = 60 °C, V = 10 mL.

Fig. 3. Effect of the temperature on the initial rate of the hydrogenation of $CaCO_3/CO_2$ catalyzed by [RhCl(mtppms)$_3$] in aqueous suspension/solution. m($CaCO_3$) = 100 mg (1 mmol), [Rh] = 1 mM, [mtppms]$_{total}$ = 4.5 mM, $p(CO_2)$ = 2 bar, $p(H_2)$ = 8 bar, V = 10 mL, t = 1 h.
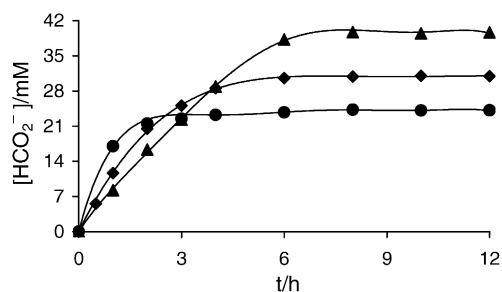
Fig. 4. Effect of the temperature on the maximum formate concentration obtained in the hydrogenation of $CaCO_3/CO_2$ catalyzed by $[RhCl(mtppms)_3]$ in aqueous suspension/solution. $m(CaCO_3) = 100\,mg$ (1 mmol), $[Rh] = 1\,mM$, $[mtppms]_{total} = 4.5\,mM$, $p(CO_2) = 2\,bar$, $p(H_2) = 8\,bar$, $V = 10\,mL$. $T = 50\,°C$ (▲), $60\,°C$ (♦), $70\,°C$ (●).

drogenation of CO_2 in aqueous solution with $K[RuCl(edta-H)]$ ($31\,kJ\,mol^{-1}$) [14], with $[RhCl(mtppts)_3]$ in the presence of amines ($25\,kJ\,mol^{-1}$) [15] and in the hydrogenation of bicarbonate with a heterogeneous Pd catalyst ($39\,kJ\,mol^{-1}$) [31]. The familiar exponential increase of the reaction rate at higher temperatures, however, involves the temperature dependence of all the component processes (solubility of CO_2, its hydration equilibrium, the dissociation equilibrium of carbonic acid, the dissolution equilibrium of $CaCO_3$ under CO_2, and the hydrogenation reaction, itself a reversible process). Therefore the activation barrier obtained from these experiments should be regarded as a composite value and cannot be related directly to the hydrogenation reaction let alone one of the steps of the catalytic cycle.

From a practical point of view, it is more important to note that the maximum available formate concentration shows an inverse dependence on the temperature (Fig. 4), so that the 20% yield observed at $50\,°C$ drops to 11% at $70\,°C$. It is reasonable to suppose that this is a consequence of the catalytic decomposition of formate (Eq. (3)). Therefore we have studied the decomposition of formate in aqueous solutions catalyzed by $[RhCl(mtppms)_3]$.

$$HCO_2^- + H_2O \rightleftharpoons HCO_3^- + H_2 \qquad (3)$$
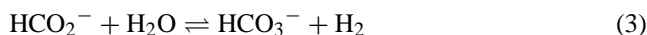
Since in most of our hydrogenation experiments we used $100\,mg$ (1 mmol) $CaCO_3$ in $10\,mL$ suspension, the decomposition studies were run using $0.1\,M\ Ca(HCO_2)_2$ solutions which corresponds to the maximum formate concentration obtainable from the above amount of $CaCO_3$. The catalyst concentration was the same both in the hydrogenation and in the decomposition experiments. One set of experiments were carried out under an inert atmosphere (Ar), while others were run under a CO_2/H_2 gas phase of the same composition and pressure used for the hydrogenations. The results are shown in Fig. 5.

Substantial decomposition of formate was observed both under Ar and under CO_2/H_2. A 6 h heating of the reaction mixture at $70\,°C$ under argon results in the complete decomposition of HCO_2^- (accompanied by the precipitation of solid $CaCO_3$) and at $50\,°C$ the extent of decomposition is
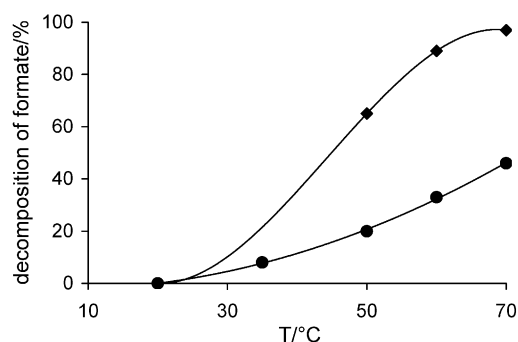

Fig. 5. Decomposition of $Ca(HCO_2)_2$ in aqueous solution catalyzed by $[RhCl(mtppms)_3]$ as a function of the temperature. $[Ca(HCO_2)_2]_0 = 100\,mM$, $[Rh] = 1\,mM$, $[mtppms]_{total} = 4.5\,mM$, $V = 10\,mL$, $t = 6\,h$, under argon (1 bar; ♦) and under carbon dioxide and hydrogen ($p(CO_2) = 2\,bar$, $p(H_2) = 8\,bar$; ●).

still 65%. Conversely, in a CO_2/H_2 atmosphere the concomitant hydrogenation of HCO_3^- formed in the decomposition reaction establishes a new equilibrium and only 46% of the initial formate is decomposed at $70\,°C$. The data of Figs. 3–5 show that although both the hydrogenation of $CaCO_3$ and the decomposition of formate is accelerated by increased temperatures, this effect is more pronounced in the case of the decomposition. This explains that at higher temperatures the hydrogenations start faster but reach a lower equilibrium formate concentration than at lower temperatures (Fig. 4).

In the investigations of the effect of the total gas pressure on the reaction rate the same gas composition, $p(CO_2):p(H_2) = 1:4$, was used which led to optimum results at $p_{total} = 10\,bar$. These studies brought an unexpected result. As seen from Fig. 6, the yields of formate at $p_{total} \geq 50\,bar$ are higher than 100% (200 mM, based on $CaCO_3$); indeed at such high pressures all the solid $CaCO_3$ goes into solution. The highest yield of HCO_2^- was 143% obtained at 100 bar pressure. The significance of this result is that the product mixture now contains free formic acid, which – in principle – can be recovered by well-established methods of the present day industrial production of formic acid [27,32].

Concerning the mechanism of the hydrogenation process, the effect of the various reaction parameters (concen-
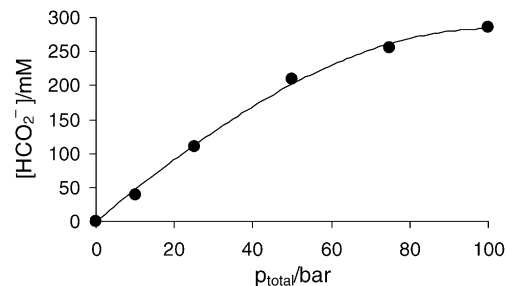

Fig. 6. Effect of the total pressure on the rate of the hydrogenation of $CaCO_3/CO_2$ catalyzed by $[RhCl(mtppms)_3]$ in aqueous suspension/solution. $m(CaCO_3) = 100\,mg$ (1 mmol), $[Rh] = 1\,mM$, $[mtppms]_{total} = 4.5\,mM$, $p(H_2):p(CO_2) = 4:1$, $T = 50\,°C$, $V = 10\,mL$, $t = 24\,h$.

tration of the catalyst, reactants, temperature) can be rationalized by assuming that it involves the free HCO_3^- produced by the dissolution of $CaCO_3$ in H_2O/CO_2. With dimethylamine as additive, Leitner et al. suggested the catalytically active species being a monohydridorhodium(I) complex $[RhH(S)(mtppts)_3]$ (S = solvent or amine) [15]. Using pH potentiometry and multinuclear NMR spectroscopy we have later established, that in aqueous solutions under H_2 the analogous $[RhH(H_2O)(mtppms)_3]$ and $[RhH_2Cl(mtppms)_3]$, the product of the oxidative addition of H_2 onto $[RhCl(mtppms)_3]$, were present in 50–50% molar ratio at pH 8.2 [33]. Since the $CaCO_3/CO_2/H_2O$ solutions are far less basic (the pH of an aqueous solution saturated with $CaCO_3$ under 1 bar of CO_2 is 5.9 [26]) it is unlikely that $[RhH(H_2O)(mtppms)_3]$ could play a significant role in the catalysis. Instead, replacement of Cl^- by HCO_3^- either before or after the oxidative addition of H_2 may give $[RhH_2(HCO_3)(mtppms)_3]$ the internal rearrangement of which could yield the product formate and regenerate the catalytically active species. A related η^2-bicarbonato species, $[RhH_2(HCO_3)(PiPr_3)_2]$ (iPr = 2-propyl) has been isolated and characterized [34]. A confirmation of this suggestion requires a detailed kinetic investigation of the hydrogenation of soluble bicarbonates catalyzed by $[RhCl(mtppms)_3]$ under conditions similar to those used in this study; this is in progress in our laboratory.

4. Conclusions

Hydrogenation of $CaCO_3$ into $Ca(HCO_2)_2$ can be achieved in aqueous suspension under a CO_2/H_2 atmosphere with the water-soluble $[RhCl(mtppms)_3]$ as catalyst. The carbonic acid dissolves $CaCO_3$ to yield solutions containing HCO_3^- which is then hydrogenated with the Rh-based catalyst. An important feature of the reaction that at high gas pressures in addition to $Ca(HCO_2)_2$ – which is obtained from 100% conversion of $CaCO_3$ – free formic acid is also produced. At the present stage this reaction suffers from several practical limitations (price of hydrogen, catalyst, separation of formic acid), nevertheless the possibility of the combined use of carbon dioxide and calcium carbonate, these abundant raw materials, remains attractive.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2004.08.045.

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