

The Kinetics of Reduction of Several Substituted Cobaloximes by Iron(II) in an Acid Medium^{1, 2}

R. Venkata Nadh, B. Syama Sundar³, and P. S. Radhakrishnamurti

Department of Chemistry, Nagarjuna University, Nagarjuna Nagar, 522510 India

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Abstract—A few cobaloximes such as pyridine-4-carboxylato bis(dimethylglyoximato) cobalt(III), pyridine-2-carboxylato bis(dimethylglyoximato) cobalt(III), benzene-1-amine-4-carboxylato bis(dimethylglyoximato) cobalt(III), benzene-1-amine-2-carboxylato bis(dimethylglyoximato) cobalt(III), and quinoline-2-carboxylato bis(dimethylglyoximato) cobalt(III) were synthesized and the kinetics of reduction of these representative cobaloximes with iron(II) in aqueous dimethyl sulfoxide-perchloric acid medium was carried out. The kinetic orders were first order in complex and first order in iron(II). H⁺ dependence was determined to be of inverse fractional order in pyridine-4-carboxylato bis(dimethylglyoximato) cobalt(III) and benzene-1-amine-4-carboxylato bis(dimethylglyoximato) cobalt(III) and of inverse first order in benzene-1-amine-2-carboxylato bis(dimethylglyoximato) cobalt(III). From the slopes and intercepts of plots of k_1 versus $1/[H^+]$, the acid-dependent and acid-independent rate constants were computed. It was observed that the acid-independent rate constants are relatively higher than the acid-dependent rate constants. This is explained as being due to the better electron mediating nature of the unprotonated form. The H⁺ dependence also shows that the possible bridging is at the oxime. This is confirmed too by the inert nature of pyridine-2-carboxylato bis(dimethylglyoximato) cobalt(III) with iron(II). Like pyridine-2-carboxylato bis(dimethylglyoximato) cobalt(III), benzene-1-amine-2-carboxylato bis(dimethylglyoximato) cobalt(III) is also inactive toward reduction, but the origin of inactivity is due to peri interaction of the first and eighth positions. The rate equation for the reduction process is

$$V = k_1 \frac{[\text{Complex}][\text{Fe}^{2+}]}{[H^+]} + k_2 [\text{Complex}][\text{Fe}^{2+}]$$

INTRODUCTION

The earliest work on the structural aspects of cobaloximes was that of Crumbliss *et al.* [1], who reported on the basis of their IR, UV, and X-ray data that the site of the protonation is dimethylglyoxime oxygen. A few cobaloximes, such as *trans*-azido pyridine- and azidoamine systems, have been subjected to kinetic study by Fe(II), and an inner sphere mechanism was postulated to explain the observed results of inverse dependence on H⁺ and the trend in the activation parameters in [2]. Independence of [H⁺] was reported in the rate of V(II) reduction of a few cobaloximes with pyridine, aniline, and ammonia as ligands in [3]. In the continuation of this work, a comparative account of Fe(II) and V(II) reduction of *trans*-diazido and dithiocyanato cobaloximes was given on the basis of a study postulating oxime bridging in these complexes [4]. The work was further extended [5] by the same authors to the Fe(II) reduction of *trans*-chloro, bromo, and iodo pyridine bis(dimethylglyoximato) cobalt(III), and the order of reactivity was found to be Co(DH)₂(Py)I > Co(DH)₂(Py)Br > Co(DH)₂(Py)Cl. In

the reduction of bromo amine substituted cobaloximes and bromo glycine cobaloximes with Fe(II), the poor sensitivity of the bromo glycine system to the variation of [H⁺] was observed in [6].

In view of the varied dependence of H⁺ in the reduction of these systems, it was thought worthwhile to study the iron(II) reduction of a few cobaloximes having pyridine-4-carboxylic acid (isonjco), pyridine-2-carboxylic acid (pico), benzene-1-amine-2-carboxylic acid (anthra), benzene-1-amine-4-carboxylic acid (PAB), and quinoline-2-carboxylic acid (quinal) as ligands in aqueous dimethyl sulfoxide and aqueous acetic acid media at various concentrations of H⁺.

MATERIALS AND METHODS

Trans-dichlorobis(dimethylglyoximato) cobaltate(III) {*trans*-[Co(dmgH)₂Cl₂]} was prepared by procedures reported earlier in the literature [7]. The method for the preparation of cobaloximes with pyridine-4-carboxylic acid, pyridine-2-carboxylic acid, benzene-1-amine-2-carboxylic acid, benzene-1-amine-4-carboxylic acid, and quinoline-2-carboxylic acid as ligands is similar to that adopted by Vijayaraghavan *et al.* [8] and others [9]. The purity of the complexes was checked by their IR spectra and by elemental analysis. All of the chemicals

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³Author for correspondence.

Table 1. Values $k_1 \times 10^4$, s^{-1} , for complexes $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ (I), $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$ (II), and $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$ (III)

[Complex] × 10 ⁴ , M	I	II	III	[Fe(II)] × 10 ³ , M	I	II	III	DMSO/H ₂ O	I	II	III	[LiClO ₄], M	I
at 2% DMSO-98% H ₂ O (v/v)													
0.25	2.003	—	2.947	0.8	1.500	—	—	0.5 : 99.5	2.723	3.837	2.403	0.01	2.648
0.50	2.104	3.880	3.160	1.6	2.723	3.837	2.403	2 : 98	1.996	3.812	3.131	0.05	2.669
1.0	1.996	3.812	3.131	3.2	3.293	3.896	5.352	5 : 95	2.070	3.300	3.473	0.1	2.723
2.0	2.626	4.031	2.887	6.4	7.500	6.954	11.501	10 : 90	—	—	4.730	0.1	2.230
4.0	2.422	—	—	12.8	—	16.323	28.275					0.1	2.281

Note: General reaction conditions: [Complex] = 1.0×10^{-4} M, $[\text{HClO}_4]$ = 10.0×10^{-2} M, solvent: 0.5% DMSO-99.5% H₂O (v/v), $[\text{Fe(II)}]$ = 1.6×10^{-3} M, $[\text{LiClO}_4]$ = 0.1 M, 30°C.

used for the preparation of the complexes and for kinetic study were of analytical reagent grade.

Kinetic measurement. Since the complexes were not soluble in water, the studies were carried out in mixtures of 0.5% DMSO-99.5% H₂O (v/v) and 0.5% AcOH-99.5% H₂O (v/v). Solutions of weighed amounts of the complexes were prepared in dimethyl sulfoxide. Solutions of the complexes with a quantity of lithium perchlorate sufficient to give 0.1 M ionic strength and ferrous ammonium sulfate solution with suitable amounts of perchloric acid and lithium perchlorate were thermostatted separately in a cell compartment and the reaction was initiated by transferring the iron(II) solution with a rapid delivery pipette into the complex solutions. Kinetics was monitored at wavelength 300 nm for the complexes on a Systronics spectrophotometer. Almost all of the experiments were carried out under pseudo-first order conditions with a 16-fold excess of iron(II). Rate constants were calculated from the slopes of the plots of $\log(D_t - D_\infty)$ versus time. All of the reactions were studied up to at least three half-lives, and the plots were linear.

Stoichiometry. The reaction mixtures containing an excess of cobaloximes over iron(II) were allowed to react in a thermostatted water bath for 24 h. The amount of iron(III) was determined colorimetrically [10]. The stoichiometry of the iron(II) reduction of the cobalt complexes was found to be 1 : 1.

RESULTS

The first-order dependence of the complex was confirmed by the perfectly linear $\log(D_t - D_\infty)$ versus time plots for the loss of the complex. This was also confirmed by studying the effect of a change in the concentration of cobaloximes at a fixed concentration of iron(II). A near constancy in first-order rate constants was observed (Table 1). The effect of varying the iron(II) concentration at a fixed concentration of cobaloximes has been studied, and the reaction was found to be first-order in iron (Table 1).

Effect of variation of solvent composition. In the reduction of $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, increasing the solvent dimethyl sulfoxide (DMSO) component in a binary mixture of DMSO and water results in the kinetic rate decrease (Table 1), indicating that the reaction rates decelerated with a decrease in the dielectric constant of the medium, whereas a slight increase in kinetic rate is observed with a decrease in the dielectric constant of the medium in the reduction of $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$. This seems to be anomalous, as factors such as hydrogen bonding and other solvent effects may be responsible for this behavior.

In experiments conducted in a 0.5% AcOH-99.5% H₂O (v/v) medium instead of a 0.5% DMSO-99.5% H₂O (v/v) one, the reaction rates are in all cases uniformly less. This confirms the fact that, when solvents of low dielectric constant are used, the reactions are retarded (Tables 1, 2). In other words, a decrease in the dielectric constant decreases the reaction rate.

Effect of added salts. The addition of salts like LiClO₄, NaClO₄, and KClO₄ have a marginal effect on the rate of reaction, indicating that these reactions are not influenced by either changing ionic strength or changing specific ions (Table 1).

Effect of varying $[\text{H}^+]$ in aqueous dimethyl sulfoxide medium. The effect of varying the concentration of $[\text{H}^+]$ on the rate of the reaction was investigated in a 0.5% DMSO-99.5% H₂O (v/v) medium. The reaction rate decreases continuously with an increase in $[\text{H}^+]$ in the reduction of $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$. However, in the reduction of $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, the reaction rate decreases until the $[\text{H}^+]$ is 2.0×10^{-2} M and the reaction is later independent of the acid concentration (Table 2).

Plots of $\log k_1$ versus $\log[\text{H}^+]$ are linear for the three complexes. The dependence on $[\text{H}^+]$ is of inverse fractional order in the two complexes $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$; it is of inverse unit order in the case of $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$. This indicates that the reactive species are free molecules in the reduction of

Table 2. Value $k_1 \times 10^4, s^{-1}$, for complexes I-III

[HClO ₄] × 10 ² , M	I	II	III	I	II	III
	0.5% DMSO-99.5% H ₂ O (v/v)			0.5% AcOH-99.5% H ₂ O (v/v)		
0.5	5.043	10.750	-	4.070	4.459	-
1.0	4.321	7.110	8.780	3.295	3.862	-
2.0	3.492	5.584	8.281	3.192	4.347	-
5.0	3.422	4.764	5.557	3.314	2.984	7.020
10.0	3.837	2.723	1.952	3.334	2.017	1.955
30.0	3.837	1.601	0.750	3.323	0.915	0.872
60.0	3.373	-	0.395	3.251	0.631	0.411
100.0	-	-	0.305	3.286	-	0.321

Note: General reaction conditions: [Complex] = 1.0×10^{-4} M, [LiClO₄] = 0.1 M, [Fe(II)] = 1.6×10^{-3} M, 30°C.

[Co(dmgH)₂(anthra)Cl], whereas the reactive species in the reduction of [Co(dmgH)₂(isonico)Cl] and [Co(dmgH)₂(PAB)Cl] are both protonated and unprotonated.

An attempt was made to evaluate the rate constants for acid-independent and acid-dependent mechanisms.

Plots of k_1 versus $1/[H^+]$ were drawn for the three systems; the corresponding intercepts and slopes were obtained for two of them, [Co(dmgH)₂(isonico)Cl] and [Co(dmgH)₂(PAB)Cl], while the slope alone was obtained for the third, [Co(dmgH)₂(anthra)Cl], as there was no intercept (Figs. 1a, 1b). This means that the equilibrium will be as follows:

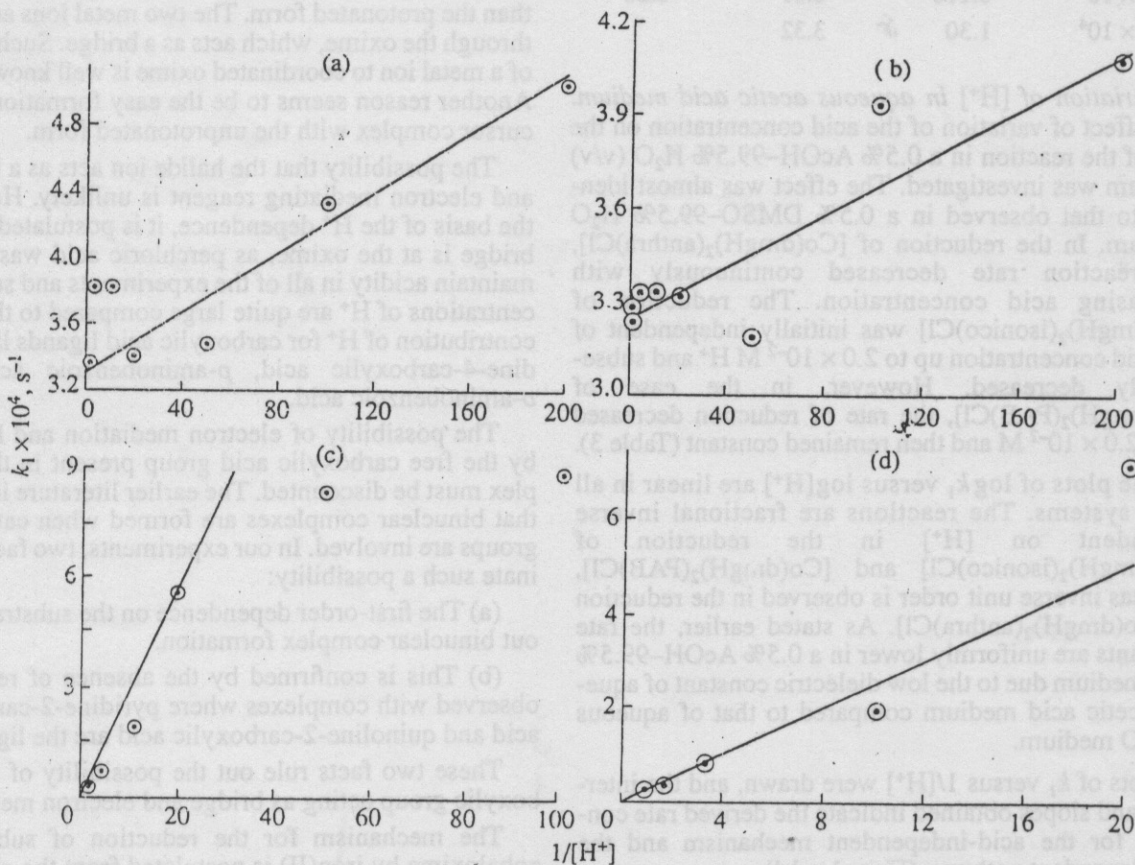
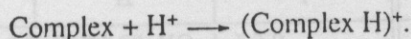


Fig. 1. The dependences $k_1 = f(1/[H])$ for 1×10^{-4} M Co(dmgH)₂(PAB)Cl (a, b) and Co(dmgH)₂(anthra)Cl (c, d) in various solvents (v/v): (a, c) 0.5% DMSO-99.5% H₂O, (b, d) 0.5% AcOH-99.5% H₂O.



The protonated complex undergoes dissociation reversibly to yield complex and H^+ . Hence, the reactive species are unprotonated and protonated complexes for the first two systems. In the last case, the protonated complex breaks down in a first-order fashion and the actual reaction is mainly between unprotonated complex and the reductant. In other words, when the breakdown of the protonated complex occurs reversibly in a fractional order fashion, both species are participating in the rate-determining step.

In the third system, the reaction will be between the unprotonated molecule and reductant exclusively, as the breakdown of the protonated complex is first-order in nature.

The following data describe the intercepts and slopes for the plots of k_1 versus $1/[\text{H}^+]$ for the three chloro cobaloximes with pyridine-4-carboxylic acid as the ligands:

Complex	I	II	III
$k_1 \times 10^4$	0.118	0.01	0.28
$k_2 \times 10^4$	1.30	3.32	

Variation of $[\text{H}^+]$ in aqueous acetic acid medium. The effect of variation of the acid concentration on the rate of the reaction in a 0.5% AcOH–99.5% H_2O (v/v) medium was investigated. The effect was almost identical to that observed in a 0.5% DMSO–99.5% H_2O medium. In the reduction of $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$, the reaction rate decreased continuously with increasing acid concentration. The reduction of $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ was initially independent of the acid concentration up to 2.0×10^{-2} M H^+ and subsequently decreased. However, in the case of $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, the rate of reduction decreased up to 2.0×10^{-2} M and then remained constant (Table 3).

The plots of $\log k_1$ versus $\log[\text{H}^+]$ are linear in all three systems. The reactions are fractional inverse dependent on $[\text{H}^+]$ in the reduction of $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, whereas inverse unit order is observed in the reduction of $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$. As stated earlier, the rate constants are uniformly lower in a 0.5% AcOH–99.5% H_2O medium due to the low dielectric constant of aqueous acetic acid medium compared to that of aqueous DMSO medium.

Plots of k_1 versus $1/[\text{H}^+]$ were drawn, and the intercepts and slopes obtained indicate the derived rate constants for the acid-independent mechanism and the acid-dependent pathway (Figs. 1c, 1d):

Complex	I	II	III
$k_1 \times 10^5$	0.812	0.022	2.4
$k_2 \times 10^4$	0.75	3.24	

Table 3. Values $k_1 \times 10^4$, s^{-1} , for complexes I and II

AcOH : H_2O (v/v)	I	II
0.5 : 99.5	2.017	3.585
2 : 98	1.884	3.536
5 : 95	1.832	–
10 : 90	1.430	–

Note: General reaction conditions: $[\text{Complex}] = 1.0 \times 10^{-4}$ M, $[\text{Fe}(\text{II})] = 1.6 \times 10^{-3}$ M, $[\text{LiClO}_4] = 0.1$ M, $[\text{HClO}_4] = 0.1$ M, 30°C .

Mechanism and rate law. The rate equation can be represented as follows on the basis of the kinetic orders observed:

$$W = k_1 \frac{[\text{Complex}][\text{Fe}^{2+}]}{[\text{H}^+]} + k_2 [\text{Complex}][\text{Fe}^{2+}]$$

It was observed that the acid-independent reaction rates are much higher than the acid-dependent reaction rates. Apparently, one of the main reasons for this is that the unprotonated form is a better electron mediator than the protonated form. The two metal ions are linked through the oxime, which acts as a bridge. Such binding of a metal ion to coordinated oxime is well known [1, 4]. Another reason seems to be the easy formation of precursor complex with the unprotonated form.

The possibility that the halide ion acts as a bridging and electron mediating reagent is unlikely. Hence, on the basis of the H^+ dependence, it is postulated that the bridge is at the oxime, as perchloric acid was used to maintain acidity in all of the experiments and such concentrations of H^+ are quite large compared to the likely contribution of H^+ for carboxylic acid ligands like pyridine-4-carboxylic acid, *p*-aminobenzoic acid, and *o*-aminobenzoic acid.

The possibility of electron mediation and bridging by the free carboxylic acid group present in the complex must be discounted. The earlier literature indicates that binuclear complexes are formed when carboxylic groups are involved. In our experiments, two facts eliminate such a possibility:

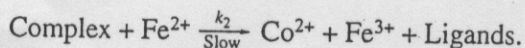
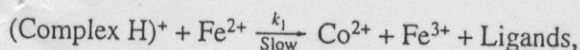
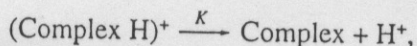
(a) The first-order dependence on the substrate rules out binuclear complex formation.

(b) This is confirmed by the absence of reduction observed with complexes where pyridine-2-carboxylic acid and quinoline-2-carboxylic acid are the ligands.

These two facts rule out the possibility of the carboxylic group acting as bridge and electron mediator.

The mechanism for the reduction of substituted cobaloxime by iron(II) is postulated from the observed kinetic orders as follows:

In the acidity range studied under experimental conditions, it is presumed that the formed complex breaks down reversibly into complex and H^+ due to inverse dependence.



Hence,

$$W = k_1 \frac{[\text{Complex}][\text{Fe}^{2+}]}{[\text{H}^+]} + k_2 [\text{Complex}][\text{Fe}^{2+}].$$

Inert nature of trans-chloro pyridine-2-carboxylato bis(dimethylglyoximato) cobalt(III) and trans-chloro quinoline-2-carboxylato bis(dimethylglyoximato) cobalt(III). The two complexes $[\text{Co}(\text{dmgH})_2(\text{pico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{quinal})\text{Cl}]$ are subjected to reduction using iron(II) as reducing agent under conditions similar to those of the iron(II) reduction of $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$, $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, and $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$.

Surprisingly, the two complexes $[\text{Co}(\text{dmgH})_2(\text{pico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{quinal})\text{Cl}]$ did not undergo reduction with iron(II), which calls for explanation. In all of the systems studied, the complexes $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$, $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, and $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$ are reduced with iron(II) in a fairly reasonable time. Assuming that nitrogen bridging with cobalt reduction involving electron transfer takes place readily as there is no structural steric inhibition by the substituent carboxyl groups present.

$[\text{Co}(\text{dmgH})_2(\text{pico})\text{Cl}]$ is a unique example in which the ring nitrogen bonding with cobalt is hindered by the *ortho* carboxyl group in the reduction process by electron transfer. Hence, no reduction takes place when carboxyl is present adjacent to the ring nitrogen. In the $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$ system, it is the carboxyl *ortho* to exocyclic nitrogen which is bound to cobalt. This system is reduced with iron(II), unlike $[\text{Co}(\text{dmgH})_2(\text{pico})\text{Cl}]$, in which ring nitrogen is involved. $[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$ and $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$ do not have structural difficulty, as the carboxyl is farther from the nitrogen bonded to cobalt. Hence, systems like

$[\text{Co}(\text{dmgH})_2(\text{isonico})\text{Cl}]$, $[\text{Co}(\text{dmgH})_2(\text{PAB})\text{Cl}]$, and $[\text{Co}(\text{dmgH})_2(\text{anthra})\text{Cl}]$ are reduced, as the substituent carboxyl group has no effect on reduction. Thus, the inert nature of $[\text{Co}(\text{dmgH})_2(\text{pico})\text{Cl}]$ is explained.

$[\text{Co}(\text{dmgH})_2(\text{quinal})\text{Cl}]$ belongs to a different category, since the carboxyl group is involved in bonding with cobalt, as can be seen from the IR spectral data when no free carboxyl group is present. Even this molecule is inert toward iron(II), probably because of the steric interaction of *peri* hydrogen to ring nitrogen, thus causing inertness in the reduction process.

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