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Kinetic analysis of non-isothermal decomposition of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} succinate complexes in a nitrogen atmosphere

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Abstract

Thermogravimetry in conjunction with differential thermogravimetry and differential scanning calorimetry, was used to investigate the kinetics of thermal decomposition of some transition metal (Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}) succinate complexes in a nitrogen atmosphere. The results indicate that diffusion processes are the decisive mechanisms for the decomposition. Values of E, Z, ΔH and ΔS were calculated for the complexes and their variation was related to variation in their structure.

INTRODUCTION

It is well known [1] that Ni^{2+} ion forms complexes of various coordination structures, e.g. octahedral, tetrahedral and square planar, depending on the ligand, and that mutual transformation often occurs among these structures. Allan et al. [2] used a dicarboxylic acid such as succinic acid to form complexes with transition metals. It has been shown [3] that the nature of the coordination atoms or molecules affects the stability of the complexes. Consequently, it is interesting to prepare the succinates of the transition metals Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} to study their thermal stability in relation to their lattice structure. A kinetic investigation on the basis of thermal analysis is an effective method of clarifying the mechanism of a solid state reaction. When a solid reaction such as thermal dehydration and decomposition is accompanied by a weight change, thermogravimetry (TG) is suitable for the kinetic analysis [4] of the reaction. Differential scanning calorimetry (DSC) is also useful in identifying the type of thermol-

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ysis reaction. The kinetic parameters for the decomposition process can be determined. This report presents the results of the study.

EXPERIMENTAL

The transition metal succinates of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} were prepared by adopting the method of Allan et al. [2], dissolving the carbonate of the metal ion in a hot solution of succinic acid. The unreacted carbonate was removed by filtration. The metal succinate was precipitated by concentrating the filtrate on a steam bath and purified by washing several times with warm water.

The concentration of the metal ion was determined using a Varian AA-1475 series atomic absorption spectrophotometer, and the carbon and hydrogen analyses were obtained using a Carlo Erba elemental analyzer model 1106. Analysis of the C, H and metal ions agreed with the values derived from the formula; the experimental data are shown in Table 1. The IR spectra were obtained using the KBr disk technique (4000–600 cm^{-1}) on a Pye Unicam SP3-100 IR spectrophotometer.

TG and DTG thermograms were recorded using a TA 3000 Mettler thermobalance with a heating rate of 10°C min^{-1}, 10 mg sample weight, 50 ml (NTP) min^{-1} of N_2 gas flow in the temperature range 50–950°C. The DSC analyzer used was a DSC-30 Mettler system with conditions as in the TG analysis, except that the final temperature was 590°C and the sample weight was 6 mg. The TG data obtained were processed using a PS/230 IBM microcomputer, with LOTUS 1-2-3 program development corporation 1989, and ENERGRAPHIC program copyright 1983 software.

RESULTS AND DISCUSSION

It is known that the reaction rate of a solid thermal decomposition can be expressed by the general equation

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{1}$$

TABLE 1

Elemental analysis of the compounds

Compound	Metal (%)		C (%)		H (%)	
	Found	Theor.	Found	Theor.	Found	Theor.
$Fe(C_4H_4O_4)\cdot 2H_2O$	26.74	26.87	23.26	23.09	3.96	3.85
$Co(C_4H_4O_4)\cdot 4H_2O$	24.12	23.86	19.13	19.44	4.89	4.86
$Ni(C_4H_4O_4)\cdot 4H_2O$	23.93	23.79	19.18	19.47	4.95	4.87
$Cu(C_4H_4O_4)\cdot 2H_2O$	30.16	29.47	21.87	22.27	3.82	3.71

TABLE 2

Kinetic equations used for the construction of the simulated decomposition reaction

Mechanism	$g(\alpha)$	Rate-controlling process
D_1	α^2	One-dimensional diffusion
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander function)
D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling–Brounshtein function)
R_n	$[1-(1-\alpha)^{1/n}]$	Phase boundary reaction $n = 1$, 2 and 3
A_m	$[-\ln(1-\alpha)]^{1/m}$	Random nucleation and its subsequent growth $m = 2$ and 3 (Avrami–Erofeev function)
f_1	$\ln(1-\alpha)$	First-order kinetics

where $f(\alpha)$ is a function depending on the actual reaction mechanism. When the temperature of the sample is increased at a constant rate $B = \mathrm{d}T/\mathrm{d}t$, we can write

$$\frac{d\alpha}{\mathrm{d}T}=\frac{A}{B}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

By integration

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{B}\int_0^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{3}$$

or

$$\ln g(\alpha)=-\frac{E}{RT}+\ln\frac{AR}{BE} \tag{4}$$

In order to test the validity of the above equations, the TG curves and the mechanisms listed in Table 2 were used, taking into account that $\alpha=(\omega_0-\omega)/(\omega_0-\omega_t)$ where ω_0, ω and ω_t are the initial, actual and final sample weights respectively.

Plotting the left-hand side of eqn. (4) against $1/T$ should give a straight line with a slope of $-E/R$, irrespective of the $g(\alpha)$ values employed. To select the $g(\alpha)$ values that best fit the actual mechanism of the studied reaction, however, the correlation coefficient r must be calculated where it will be very near to unity, in accordance with the result of Criado et al. [5]. Once the mechanism is established, the pre-exponential factor can be calculated.

TABLE 3

IR spectra of transition metal succinates (4000-600 cm^{-1})

Compound [a]	ν(O – H) (H_2O)	ν(COOH)	ν(COO^-)
$C_4H_6O_4$		1680 (s)	
$Fe(C_4H_4O_4)\cdot 2H_2O$	3500–3100 (br, s)		1580 (s)
$Co(C_4H_4O_4)\cdot 4H_2O$	3250–2950 (br, s)		1540 (s)
$Ni(C_4H_4O_4)\cdot 4H_2O$	3220–2950 (br, s)		1540 (s)
$Cu(C_4H_4O_4)\cdot 2H_2O$	3600–3200 (br, s)		1610 (s)

[a] $C_4H_6O_4$, succinic acid; $C_4H_4O_4^{2-}$, succinate di-anion; s, strong; br, broad.

IR spectra

The IR spectra showed frequencies corresponding to carboxylate group, hydroxyl group, metal–oxygen bond etc., and to the bidentate linkage of the carboxylate group with the metal. These vibrations were observed on the basis of the difference between the anti-symmetric stretching and symmetric stretching frequencies. The wavenumbers of the IR absorption bands as well as their description and assignments are given in Table 3. Although the table does not give complete details, an IR absorption band in the region 1600–1500 cm^{-1} is assigned to the stretching vibration of the carboxylic groups linked to the metal ions [6]. Also, an absorption band in the region 3600–2900 cm^{-1} indicates the presence of water of crystallization [7].

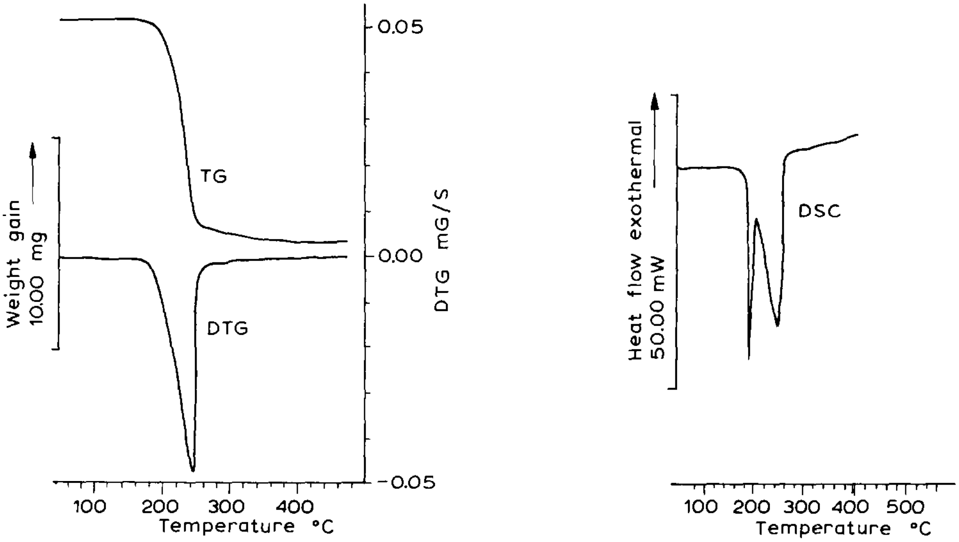

Fig. 1. TG, DTG and DSC curves for pure succinic acid.

The thermal decomposition of Fe, Co, Ni and Cu succinates indicates two major distinct processes. The first includes a dehydration process, the second leads to decomposition of the succinate. The TG curves showed weight loss in the range 90–147°C corresponding to elimination of the water molecule combined with the complexes. The number of water molecules depend entirely on the nature of the complex structure and also on the drying procedure [8]. The TG temperature range for the decomposition process started at 150°C and ended around 440°C. Allan et al. [3] studied these types of complex using electronic, spectral and magnetic measurements, and drew conclusions about the lattice structures of some of these complexes. The Ni^{2+} and Cu^{2+} complexes show a high degree of ionic character in the metal–ligand bond and the succinates were considered to have a planar arrangement with each carboxylate group on each molecule of the succinate bonded to two different metal atoms so give a chain-like structure. Also, the metal atom is bonded to metal atoms in adjacent layers by the carboxylate groups of the bridging succinate molecules to give a six-coordinated environment of the metal ion. The water molecules are attached by hydrogen bonding in each compound. The cobalt succinate has a dimeric structure, with the carboxylate group in each molecule bonded to two different cobalt atoms so that each cobalt atom is in a tetrahedral environment.

The variation in the TG, DTG and DSC data can be interpreted from the differences in the lattice structures. TG curves can be studied in more detail using the kinetic mechanisms as in Table 2. The decomposition products of the succinates were analyzed by Venkatarmann et al. [9] using

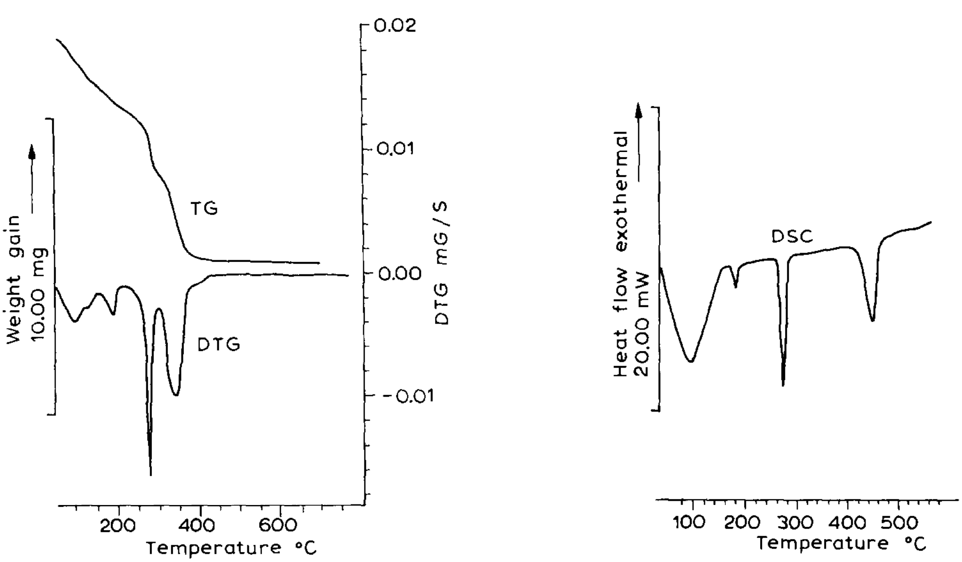

Fig. 2. TG, DTG and DSC curves for iron succinate complex.

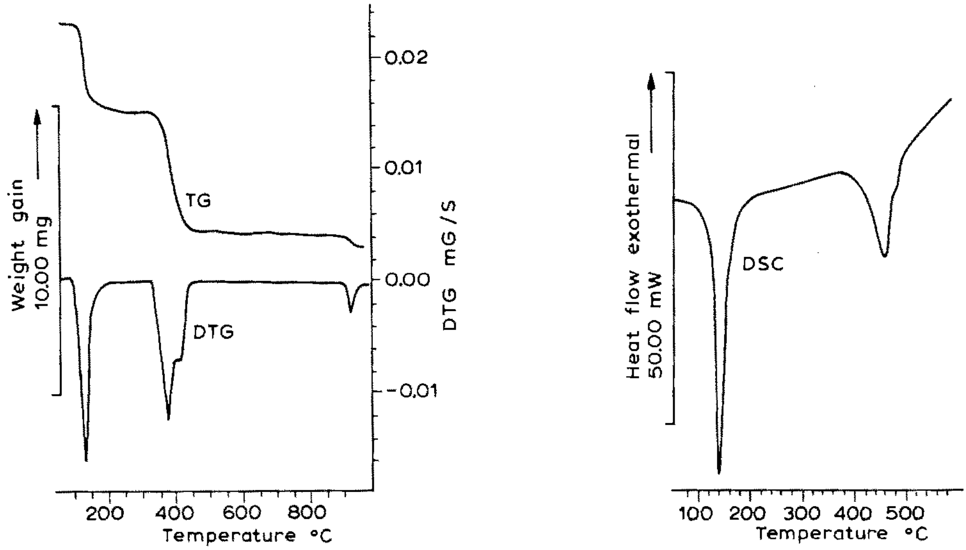

Fig. 3. TG, DTG and DSC curves for cobalt succinate complex.

chromatographic analysis. They detected different products with CH_4, $CH_2=CH_2$, C_3H_8 and CO_2 as the major products, and C_4H_8 and C_5H_{12} as minor products.

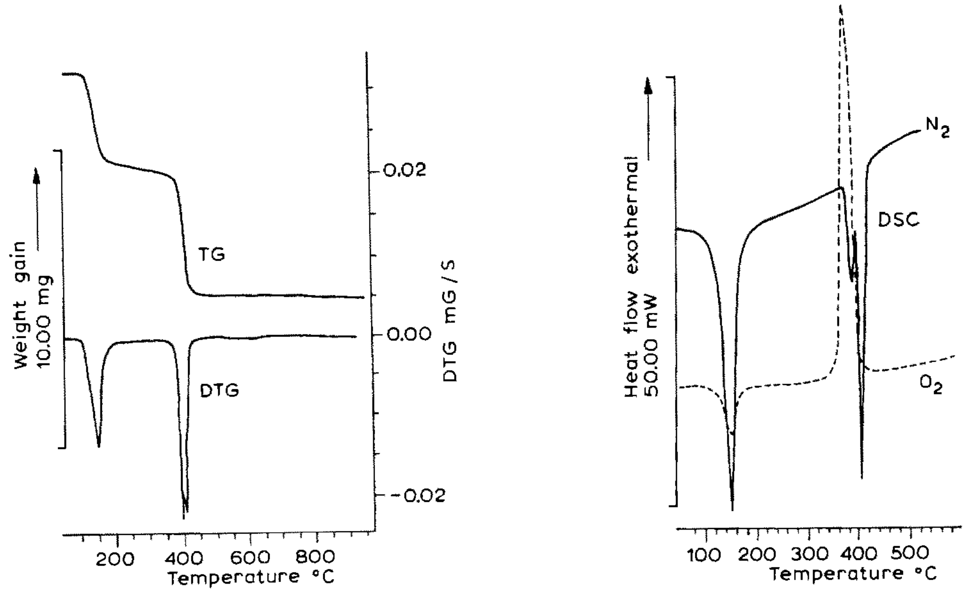

Fig. 4. TG, DTG and DSC curves for nickel succinate complex.

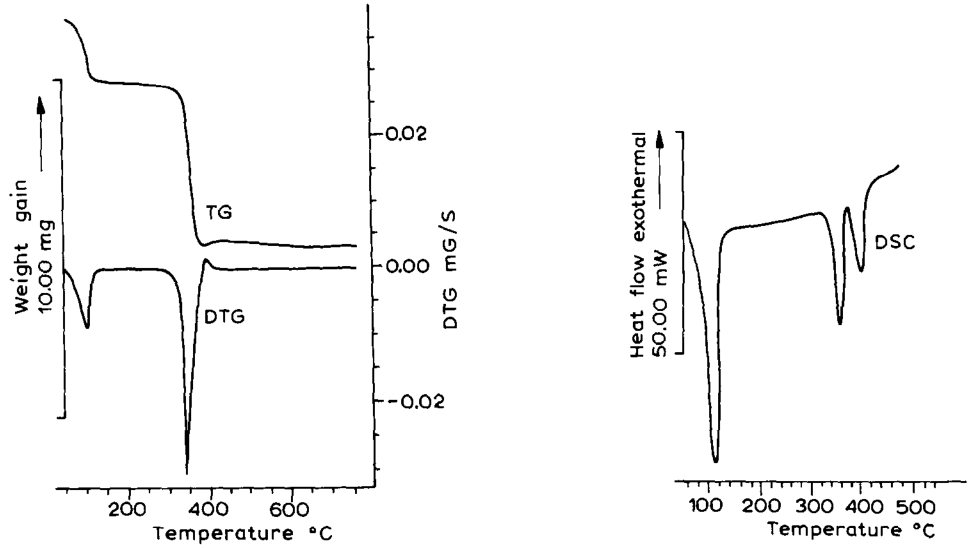

Fig. 5. TG, DTG and DSC curves for copper succinate complex.

TABLE 4

TG data for the decomposition of succinates of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} under N_2 atmosphere (50 ml (NTP) min^{-1})

Fragment decomposed	Loss found (%)	TG max. temp. (°C)
$Fe(C_4H_4O_4)\cdot 2H_2O$		
2 mol H_2O	15.9	90
1 mol CH_4	8.0	186
1 mol CO_2	19.0	276
1 mol C_2H_4 + 1 mol C_3H_8	26.8	340
Total decomposition (%)	69.7	
$Co(C_4H_4O_4)\cdot 4H_2O$		
3.6 mol H_2O	26.7	131
1 mol CH_4 + 1 mol C_3H_8	23.6	380
1 mol CO_2	16.2	396
	3.5	927
Total decomposition (%)	70	
$Ni(C_4H_4O_4)\cdot 4H_2O$		
4 mol H_2O	31.1	147
1 mol CH_4 + 1 mol C_3H_8	40.5	396
1 mol CO_2	2.3	440
Total decomposition (%)	73.9	
$Cu(C_4H_4O_4)\cdot 2H_2O$		
2 mol H_2O	17.0	104
1 mol CH_4 + 1 mol C_3H_8 + 1 mol CO_2	48.3	345
Total decomposition (%)	65.3	

TABLE 5

Kinetic parameters calculated by analysis of α values corresponding to the decomposition of the complexes according to the mechanisms shown in Table 2

$g(\alpha)$ employed	E (kJ mol^{-1})	A (s^{-1})	r
$Fe(C_4H_4O_4)\cdot 2H_2O$			
D_1	40.36	8.2×10^{4}	0.9402
D_2	53.86	6.7×10^{4}	0.9598
D_3	70.54	5.4×10^{5}	0.9612
D_4	59.80	5.98×10^{4}	0.9615
$R_{n=1}$	7.939	1.13×10^{5}	0.9190
$R_{n=2}$	26.67	2.62×10^{5}	0.9476
$R_{n=3}$	30.52	6.9×10^{4}	0.9489
$A_{m=2}$	15.04	4.09×10^{4}	0.9087
$A_{m=3}$	6.87	2.00×10^{4}	0.8230
F_1	39.31	7.17×10^{4}	0.9446
$Co(C_4H_4O_4)\cdot 4H_2O$			
D_1	55.71	8.68×10^{4}	0.9539
D_2	74.36	1.59×10^{5}	0.9748
D_3	10.36	1.62×10^{4}	0.9891
D_4	83.97	7.8×10^{4}	0.9820
$R_{n=1}$	22.33	6.0×10^{4}	0.9281
$R_{n=2}$	38.98	8.93×10^{4}	0.9802
$R_{n=3}$	46.38	9.68×10^{4}	0.9862
$A_{m=2}$	26.18	6.60×10^{4}	0.9826
$A_{m=3}$	13.85	3.9×10^{4}	0.9728
F_1	63.69	1.23×10^{4}	0.9878
$Ni(C_4H_4O_4)\cdot 4H_2O$			
D_1	37.76	8.94×10^{4}	0.9644
D_2	53.91	9.82×10^{4}	0.9643
D_3	72.27	7.72×10^{4}	0.9625
D_4	59.85	1.15×10^{5}	0.9637
$R_{n=1}$	15.43	1.99×10^{5}	0.9501
$R_{n=2}$	26.01	6.96×10^{4}	0.9544
$R_{n=3}$	30.60	7.98×10^{4}	0.9548
$A_{m=2}$	15.27	1.87×10^{5}	0.9396
$A_{m=3}$	5.63	1.17×10^{4}	0.9216
F_1	41.41	8.2×10^{4}	0.9543
$Cu(C_4H_4O_4)\cdot 2H_2O$			
D_1	108.4	2.5×10^{5}	0.9899
D_2	131.4	3.81×10^{5}	0.9898
D_3	168.3	5.78×10^{5}	0.9890
D_4	143.0	4.28×10^{5}	0.9896
$R_{n=1}$	49.0	8.07×10^{4}	0.9881
$R_{n=2}$	69.99	7.6×10^{4}	0.9882
$R_{n=3}$	78.89	1.7×10^{4}	0.9878
$A_{m=2}$	45.66	7.54×10^{4}	0.9836
$A_{m=3}$	27.10	6.061×10^{4}	0.9802
F_1	101.76	2.3×10^{5}	0.9862

TABLE 6

Enthalpies and entropies of metal succinate complexes

Type of metal succinate	ΔH_{total}	ΔH_{dehyd}	T_{max}	ΔS
$Fe(C_4H_4O_4)$	3929.6	525	377.9	−124.9
$Co(C_4H_4O_4)$	4296	854	413.8	−167.1
$Ni(C_4H_4O_4)$	4366	755	426.6	−120.5
$Cu(C_4H_4O_4)$	4104	631	385.5	−113.2

Figures 1–5 show the TG, DTG and DSC thermograms for succinic acid and the complexes, and Table 4 gives the TG analyses of the complexes under investigation.

Non-isothermal kinetic studies for the TG curves adopting the mechanisms in Table 2 reveal (see Table 5) that the predominant mechanisms for the dehydration and decomposition processes at α values less than 0.7 from the best fit are obtained with D_4 and D_3 for iron succinate, D_3 and D_4 for cobalt succinate, and D_1 and D_2 for nickel and copper succinates. Activation energies calculated from the temperature dependence of the rate constant on the basis of diffusion-controlled reaction are given in Table 5.

The DSC thermograms showed satisfactory agreement with the TG analysis. When oxygen was used instead of nitrogen for the flow gas, the endothermic decomposition peak of the complexes became exothermic, as in Fig. 3; this can be compared with the result reported by Allan et al. [2]. It could be suggested that when oxygen is used, an oxidative decomposition takes place, with heat being evolved.

The enthalpies of dehydration and decomposition, ΔH_{total}, as well as the enthalpies of dehydration, ΔH_{dehyd}, are cited in Table 6 with their calculated entropies, ΔS. The results show that ΔH_{total} increases in the order Fe succinate < Co succinate < Ni succinate, and then decreases for Cu succinate. This can be interpreted according to the difference in their lattice structures. The values of ΔS are negative after the dehydration process which reflects a more ordered structure, in the activated complexes.

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