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Model Studies of the Interaction of CO and H_2 on Transition Metals

II. On the Role of Chemisorption Complexes in Primary Reactions*

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The binding energies and electronic structures of the chemisorption complexes of CO-H_2 mixtures on iron, cobalt and nickel were calculated by means of the extended Hückel theory (EHT) within a simple chemisorption model, followed by a Mulliken [*J. Chem. Phys.* 23, 1833 (1965)] population analysis. Complexes of the Anderson type containing oxygen seem to be stable on iron and cobalt only, whereas a complex on nickel is probably of methylene type. Using the iron complex as an example, a special catalytic activity for chain propagation on (111)-surface clusters can be deduced from the geometrical and electronic structure of the complex. A comparison of the calculated structures of the iron, cobalt and nickel complexes and their probable chemical properties leads to some meaningful reflections on reaction paths during synthesis.

1. INTRODUCTION

One of the main problems in catalysis is a systematic description of catalytic systems that allows a splitting of global experimental results into a set of discrete catalytic effects. There seems to be a need of theoretical studies of pure effects on model catalysts which, confirmed by experimental results, would permit a better understanding of catalytic reactions.

In previous papers (*1*, *2*) the energetic effects of interaction of N_2, CO and H_2 with first row transition metals were analyzed. It was pointed out that semi-empirical quantum-mechanical methods, in connection with simple chemisorption models, may give a qualitive description of the first step of a catalytic reaction on a surface, namely the activation of the reactants.

In this paper an attempt is made to interpret the second step of reaction, the formation of surface complexes, using the hydrogenation of CO on iron, cobalt and nickel as an example. On the basis of a theoretical study of these complexes, some possible reaction paths leading to the well-known product distribution of this hydrogenation are discussed. First some remarks are given on the model system and the computational techniques used.

2. MODEL SYSTEM

At present, the quantum-mechanical treatment of catalytic systems, which represent a rather complex amount of catalyst atoms and chemisorbed molecules, can be done with a reasonable computing expense only by semi-empirical methods within model systems (*3*). Furthermore, if there are transition metals in this system, only techniques based on the "extended Hückel theory" (EHT) (*4*, *5*) and the "complete neglect of differential overlap" (CNDO/2) (*6*), admitting the introduction of 3*d*-electrons, will give any results. Since these methods are relatively simple, only simple models should be constructed so as not to "overextend" the method. In any case, the main physical and chemical properties of the catalyst should be included in the model.

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* Part I: Ref. (*2*).

Purely theoretical approaches to catalytic problems, starting from first principles, are still lacking. There have been some attempts to represent the metal catalyst by models developed from solid state theory (*7–9*), and these have been particularly successful in explaining bulk properties of metals. In considering surface reactions, however, the chemical reactivity of the transition metals and the alteration of surface properties during interaction in catalytic systems should not be neglected. Owing to the fact that increasing perturbation of the metal lattice is accompanied by higher catalytic activity (*10*, *11*, *31*), recently a simple model (*2*) was suggested considering as extremely perturbed surface a single metal atom with localized electrons surrounded by molecules forming a chemisorption complex. This model is not so rough as it seems, since it takes into account the serious perturbation of the lattice due to the formation of a surface (*12*, *13*). This perturbation effects a localization of electron states near the surface and may even produce special surface states with electrons localized at the surface (*14*). It is, in a first approximation, not quite clear whether these states are coupled with the periodicity of the surface or with its perturbations. Considering the structural and electronic properties of the surface, it can be shown that an ideal surface only displays nonlocalized states, whereas a perturbation produces additional localized states (*15*). The wave functions of localized states at the top of the 3*d*-band, being highly contracted and even a little more localized than free atom *d*-functions, are very similar to those of the free atom (*16*). Primary catalytic effects seem to be connected with these localized states, since the catalytic activity increases with surface perturbation, as pointed out above. There is some probability, too, that the formation of surface dipoles during chemisorption will induce an additional localization of metal electrons at the surface (*17*), so the electron states of the transition metals in chemisorption complexes can be considered to a fair approximation as localized. Therefore, if surface reactions within our simple model are studied, the interaction of surface complexes is investigated. We represent, similar to other authors (*18*, *19*), the surface in the very moment of interaction as a single atom, or a simple array of atoms in the surface geometry, with localized electron states. This corresponds extensively to the surface model concept of Fassaert, Verbeek and Van der Avoird (*41*) where surface clusters are obtained by truncating crystal clusters such that the adsorption sites have the nearest neighbor environment of an atom on the different crystallographic surfaces.

3. CALCULATIONS

All EHT calculations have been made with a FORTRAN-program using the original formalism of Hoffmann (*4*) and a parametrization by Clementi (*20*). A conventional value of $K = 1.75$ has been chosen for the Wolfsberg–Helmholtz (*21*) constant. The method is well known and described elsewhere (*4*, *5*, *22*, *40*).

Binding energies between two centers of surface complexes or between functional groups in reference to energies at large separations (100 Å) were calculated by varying the geometry of the complex (*1*, *2*). This procedure may yield as in the present case ionic reference states unless the electrons are redistributed. Discussing only the relative stability of different structures, this effect is assumed to be of minor importance and therefore neglected. First, we have adjusted all bond angles after formulating a structure similar to that of the chemisorption complex of Anderson, Hofer and Storch (*23*) with conventional bond lengths and angles of functional groups, adopting 1.3 Å as the C–O distance, a value reported from similar carbene–carbonyl complexes in homogeneous systems (*24*). To that purpose, the complex was arranged in one plane perpendicular to the x–y plane (Fig. 1). After transformation into spherical coordinates and varying the angles θ and Φ of functional groups or atoms relative to the fixed complex, optimal bond angles were found at binding energy minima. Optimal bond lengths of these functional

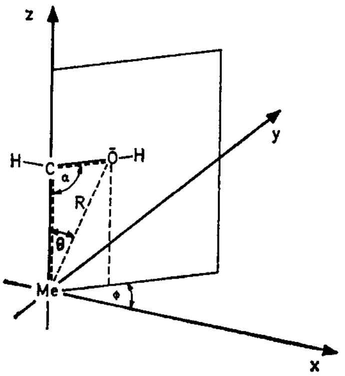

FIG. 1. Arrangement of the complexes in Cartesian coordinates. R, θ and Φ are the spherical polar coordinates, and α is the bond angle.

groups were next calculated in order to find the absolute binding energy minimum of a given arrangement. The procedure is demonstrated in Figs. 2–5.

All calculated bond lengths may be a little too short (about 0.3 Å, depending on atom types), since the EHT method does not take into account Coulomb forces; however, the bond angles can be assumed to be accurate (*22*).

The EHT calculations were followed by a Mulliken (*25*) population analysis which makes possible the calculation of the occupation of atomic orbitals, of the reduced overlap population, which is a measure of bond orders (*26*), and of the number of electrons on a given atom. This analysis enabled us to make some statements on the electronic structure of the complexes.

4. RESULTS AND DISCUSSION

One of the fundamental problems in catalysis is the identification of chemisorption complexes which guide a catalytic reaction in a desired direction (*3*). In the special case of hydrogenation of CO on transition metals, Anderson, Hofer and Storch (*23*), have formulated a chemisorption complex in order to explain the mechanism of the Fischer-Tropsch synthesis, where the chain propagation may occur by successive condensation steps of these complexes (*2*, *27*, *28*). There have been, since then, several experimental attempts to identify such complexes, but although their existence was shown by Blyholder and Neff (*29*) and by Kölbel, Patzschke and Hammer (*28*) for iron and by Balaji Gupta, Viswanathan and Sastri (*30*) for cobalt, no statements about the binding energy and the electronic structure have been made. Therefore, we have calculated this binding energy and structure of the complexes of iron, cobalt and nickel.

For this purpose, all bond lengths and angles had to be optimized in order to describe the structural changes of the complexes during chemisorption. The results show that all atoms are coplanar (Fig. 2) and that the C–O–H group is arranged in a line. This would be possible only if the C–O bond is, at least partially, of double

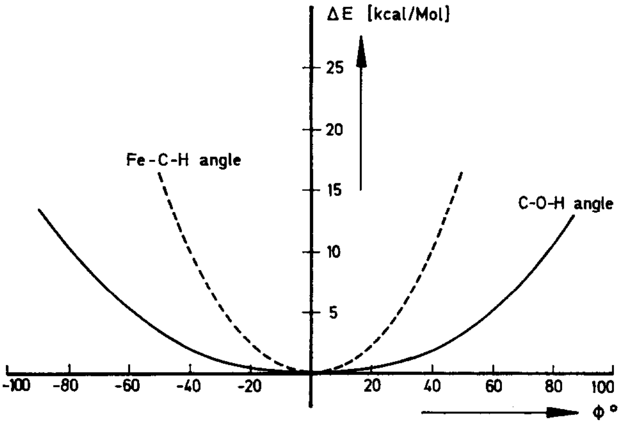

FIG. 2. Dependence of the binding energy of the iron complex on the deviation Φ out of the x–z plane.

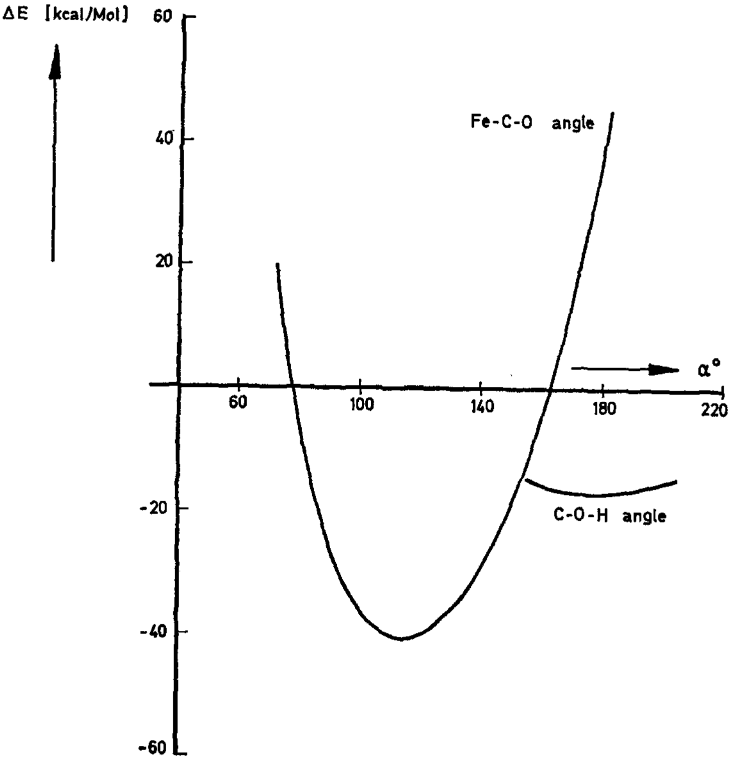

Fig. 3. Optimal bond angles of functional groups containing oxygen (iron complex as an example).

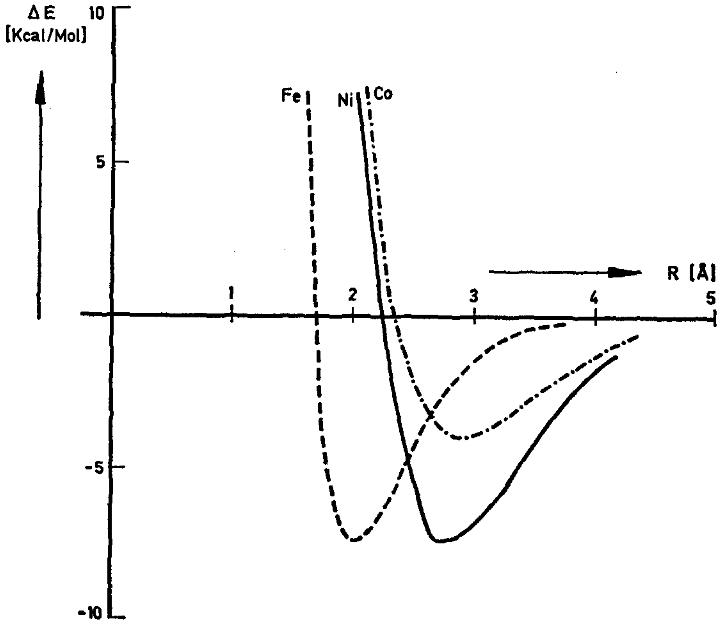

Fig. 4. Binding energy of the metal-carbon bond of the iron, cobalt and nickel complexes.

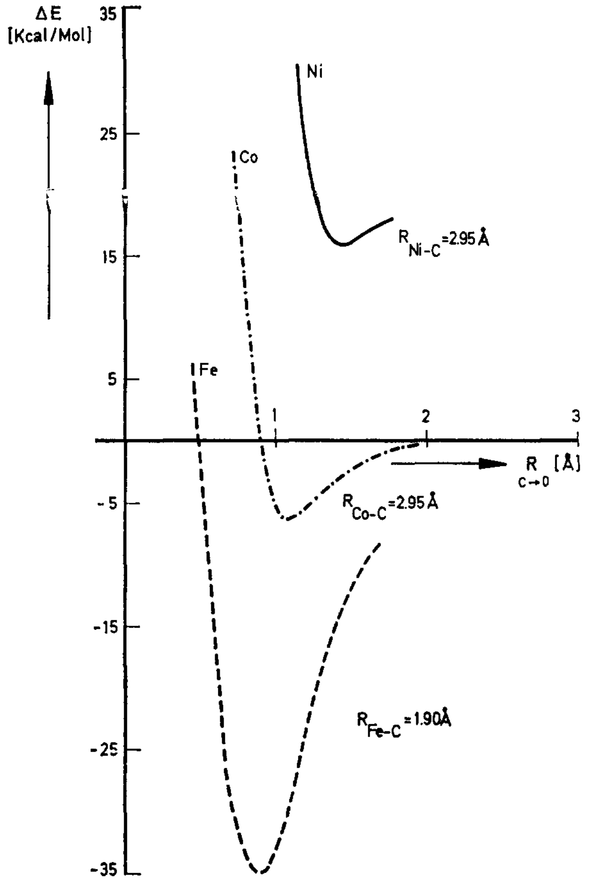

FIG. 5. Binding energy of the carbon–oxygen bond of the iron, cobalt and nickel complexes.

bond character, because sp^2-hybrids of carbon are of that planar structure. This result will have to be discussed after calculation of optimal bond lengths.

When discussing particular properties of surface complexes, mainly the metal–carbon and carbon–oxygen bonds are of special interest. Results for the calculation of optimal bond lengths are presented in Figs. 4 and 5. Figure 4 shows that chemisorption complexes display their shortest metal–carbon bond length and highest binding energy on iron. Figure 5 shows that no stable complex containing oxygen can be formed with

TABLE 1

REDUCED OVERLAP POPULATION MATRIX AND NET CHARGES OF THE IRON CHEMISORPTION COMPLEX

Atom	Fe	C	H	O	H
Fe	9.652	0.101	−0.002	−0.021	0.001
C	0.101	1.392	0.357	0.533	−0.032
H	−0.002	0.357	0.543	−0.021	0.002
O	−0.021	0.533	−0.021	5.866	0.244
H	0.001	−0.032	0.002	0.244	0.224
Charges (a.u.)	−1.731	1.649	0.122	−0.602	0.563

TABLE 2
REDUCED OVERLAP POPULATION MATRIX AND NET CHARGES OF THE COBALT CHEMISORPTION COMPLEX

Atom	Co	C	H	O	H
Co	10.031	0.034	−0.004	−0.004	0.001
C	0.034	2.123	0.363	0.382	−0.027
H	−0.004	0.363	0.508	−0.018	0.001
O	−0.004	0.382	−0.018	6.193	0.242
H	0.001	−0.027	0.001	0.242	0.210
Charges (a.u.)	−1.057	1.126	0.151	−0.795	0.575

nickel. This fact implies that no chain propagation within a condensation mechanism can occur on nickel catalysts, although it is known that these catalysts produce hydrocarbon chains of moderate lengths at relative low temperatures and pressures (*32*, *33*). Probably, there is a different reaction mechanism than that on iron and cobalt. The primary complexes on nickel are of a methylene structure, and the chain may grow by polymerization mechanisms on planes with an optimal nickel–nickel distance for that purpose. This will be the subject of another publication. In any case, the lack of –OH groups on nickel is confirmed by the experimental work of Blyholder and Neff (*32*).

In the case of iron and cobalt complexes, the carbon–oxygen bond lengths seem to be very short, but if, as mentioned above, a value of 0.3 Å is added, the resulting lengths of about 1.2 and 1.3 Å are in good agreement with those reported from homogeneous systems (*24*). The reduced overlap population will give further information on the binding character (Tables 1 and 2). In iron complexes higher values for the iron–carbon and carbon–oxygen bond (both values indicating partial double bond character) can be found. This fact agrees with reflections made above on the structure of the complexes. A relatively short carbon–oxygen bond length and partial double bond character in both complexes points to an enolic behavior, the iron complexes being more stable and enol-like. The structure of the complexes with optimized bond lengths and angles are shown in Table 3. There is another interesting fact to be reported: the atomic functions between metal and oxygen seem to have antibonding character, expressed by negative values of overlap integrals and values for the overlap population matrix (Tables 1 and 2). Meanwhile, this repulsive effect, at least on iron and cobalt, is overcompensated by a strong metal–carbon and carbon–oxygen interaction so that the complexes remain stable. In any case, a strong surface dipole with weakened intramolecular binding forces is formed. This means that these complexes are highly reactive.

If we are discussing condensation mechanisms, we have to find out optimal arrangements of two complexes on a crystal surface cluster. This is demonstrated below for iron complexes, as an example.

The complex has a large size in relation to the lattice constant a_0 of α-iron of 2.86 Å. Taking into account that it will not be stabilized either by an iron–oxygen bond or by hydrogen atoms on the nearest neighbors, no arrangement in a line nor in parallel that would favor the splitting of water can be found on 100 and 110-planes.

TABLE 3
GEOMETRICAL STRUCTURE OF THE IRON AND COBALT CHEMISORPTION COMPLEXES

	Bond lengths (Å)		Bond angles (°)		
Metal	R_{Me-C}	R_{C-O}	Me–C–H	Me–C–O	C–O–H
Fe	1.90	1.18	108	118	180
Co	2.95	1.33	109	119	180

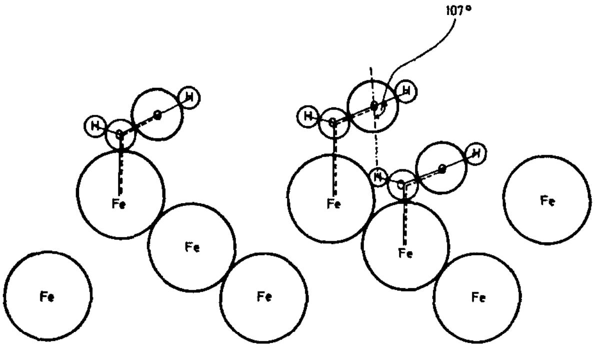

FIG. 6. Perpendicular cut through an iron (111) surface. Left side: optimal arrangement of a single chemisorption complex; right side: two chemisorption complexes stabilizing one another.

On 111-planes, a stabilization by additional iron–carbon interaction can be observed, if the complex is arranged such that the oxygen atom is situated above the first surface hole where the next iron atom is situated 1.65 Å beneath the plane (Fig. 6) (Table 4). A stabilization is also possible by arranging two complexes one above the other, as shown at the right side of Fig. 6 (see Table 5). The reduced overlap population analysis (Table 5) indicates that the electron density of the iron–carbon bond of the lower complex situated in the surface hole increases considerably, indicating a very stable bond, while the carbon–oxygen bond remains nearly unchanged. An increased iron–carbon bond length from 1.9 to 2.4 Å for the upper complex leads to an energy gain of about 4 kcal and the migration of the proton of the lower –OH group to the top resulting in a C–O–H bond angle of about 130° to an additional gain of about 9 kcal. Both –OH groups are stable, the upper one having a higher binding energy. An optimal H–OH bond angle for the splitting of water is preformed with the –OH group of the upper complex, as can be seen from Fig. 6, but there is only a repulsive interaction. The splitting of water may rather occur by interaction of the lower –OH group. These results point to a special catalytic activity of the 111-plane [see also (*34*)].

The carbon–carbon interaction of the complexes seems to be weak, so the first step of chain propagation may occur only after splitting of water. An aldehyde and a methylene functional group are then left on the surface close to one another. Since for thermodynamic reasons formaldehyde cannot be a product of the synthesis, expected primary reaction products will be

TABLE 4

REDUCED OVERLAP POPULATION MATRIX AND NET CHARGES OF A STABILIZED IRON CHEMISORPTION COMPLEX ON A (111)-SURFACE CLUSTER[a]

Atom	C	H	O	H	Fe	Fe
C	1.294	0.274	0.523	−0.031	0.179	0.002
H	0.274	0.382	−0.009	0.000	0.013	−0.000
O	0.523	−0.009	5.831	0.242	−0.031	0.001
H	−0.031	0.000	0.242	0.220	−0.001	0.000
Fe	0.179	0.013	−0.031	−0.001	8.479	0.047
Fe	0.002	−0.000	0.001	0.000	0.047	9.376
Charges (a.u.)	1.760	0.340	−0.556	0.560	−0.687	−1.426

[a] See left side of Fig. 6.

TABLE 5

Reduced Overlap Population Matrix and Net Charges of Two Iron Chemisorption Complexes on a (111)-Surface Cluster, One Stabilizing Another[a]

Atom	Lower complex					Upper complex				
	Fe	C	H	O	H	Fe	C	H	O	H
Fe	9.599	0.141	0.003	−0.029	0.001	0.001	0.001	−0.001	−0.001	−0.000
C	0.141	1.451	0.306	0.530	−0.032	0.002	0.004	−0.001	−0.003	−0.002
H	0.003	0.306	0.464	−0.017	0.001	0.039	0.036	−0.002	−0.007	−0.001
O	−0.029	0.530	−0.017	5.904	0.242	−0.004	−0.000	0.000	0.000	0.000
H	0.001	−0.032	0.001	0.242	0.224	0.001	0.000	−0.000	−0.000	0.000
Fe	0.001	0.002	0.038	−0.004	0.001	9.685	0.046	−0.008	−0.013	0.001
C	0.001	0.004	0.036	−0.000	0.000	0.046	1.425	0.357	0.533	−0.032
H	−0.001	−0.001	−0.002	0.000	−0.000	−0.008	0.357	0.534	−0.021	0.002
O	−0.001	−0.003	−0.007	0.000	−0.000	−0.013	0.533	−0.021	5.855	0.243
H	−0.000	−0.000	−0.001	0.000	0.000	0.001	−0.032	0.002	0.243	0.224
Charges (a.u.)	−1.715	1.602	0.179	−0.627	0.564	−1.749	1.630	0.139	−0.586	0.565

[a] See right side of Fig. 6.

methane by total hydrogenation, ethene by partial hydrogenation and acetaldehyde by desorption and recombination of surface complexes.

These possible reaction paths can be confirmed by experimental work. A formulation of reaction mechanisms involving acetaldehyde as intermediate product has been given by Bashkyrov *et al.* (*35*) and worked out recently (*36*), explaining also the synthesis of amines in presence of ammonia (*37*). This accords with experimental results by which it becomes obvious that acetaldehyde, acrolein, and C_2–C_3 olefines are obtained as primary products of synthesis at pressures of about 10^{-6} Torr and temperatures of 70–120°C on iron catalysts (*38*).

Being aware of the simplicity of the chemisorption model and the quantum-mechanical methods used a comparison of the calculated properties of the chemisorption complexes displays some interesting parallels to the synthesis properties of iron, cobalt and nickel. The higher stability and strongly marked enolic behavior of the iron complex relative to the cobalt complex seems to be responsible for the production of longer hydrocarbon chains with a higher content of oxygenated species in the product spectrum on iron. Since iron seems to adsorb molecular hydrogen at a high rate beside atomic hydrogen (*2*, *39*), the hydrogenation rate should be lower than on cobalt catalysts, explaining together with the high stability of the complex the considerable amount of olefins in the synthesis products of iron. The fact that there is only low probability for an oxygen-containing complex on nickel catalysts implies that there should be no oxygenated reaction products on this catalyst. Taking into account the excellent hydrogenation properties of nickel, one only can expect paraffinic products of moderate chain lengths on this catalyst.

Since these statements are in good agreement with experience in the hydrogenation of CO on iron, cobalt and nickel, we are encouraged to continue this work on the principles of heterogeneous catalytic reactions on transition metals.

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