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A comparative study of the bond strengths of the second row transition metal hydrides, fluorides, and chlorides

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Summary. Correlated calculations have been performed for the diatomic second row transition metal hydrides, fluorides, and chlorides. The ground states have been determined for the entire second row from yttrium to palladium. It is found that the halide binding energies vary much more across the row than the hydride binding energies. The results are analyzed in terms of ionic and covalent contributions to the bonding. The two main factors responsible for the large variation of the halide binding energies are differences in ionization energies and differences in the interactions between the halide lone-pairs and the metal 4*d*-orbitals for the atoms to the left and to the right. To the left the lone-pair interaction is attractive through electron donation to empty 4*d*-orbitals, whereas to the right the interaction is repulsive.

Key words: Transition metal hydrides, fluorides, chlorides – Ground states – Bond strength

1. Introduction

The understanding of the reactivity of transition metal complexes is, because of the important catalytic implications, an intense research area of modern chemistry, see for example [1]. By tradition, theoretical work has closely followed the experimental work and focussed on special systems, which have been shown to be of particular interest, see for example [2]. In recent years a more systematic approach towards the understanding of the properties of transition metal complexes has started to develop. This approach starts with the understanding of the bonding and reactivity of naked transition metal atoms and treats sequences of atoms simultaneously, typically a whole row of the periodic table [3, 4]. Recent work of this type have been the studies of the reactivity of the second row transition metal atoms with methane [4], ethylene [5], ethane, cyclopropane, and cyclobutane [6]. As a natural continuation of this work ligands have been added to the transition metals in order to study their effects on the reactivity. A first step in this direction has been the study of the effect on the oxidative addition of methane of adding hydride ligands to second row transition metal atoms [7]. This will be followed by a study focussed on a comparison of the effects of hydride ligands and the effects of adding stronger electron acceptors like fluorides and chlorides. In a first step of this study the diatomic transition metal fluorides and chlorides have been studied as the simplest examples of this type of metal ligand bonding. The results of this initial study will be presented here. Even though the diatomic molecules by themselves are of limited catalytic interest, it has been shown [3] that systematic studies of sequences of transition metal diatomic molecules is a very efficient way to understand and quantify the main effects involved in the bonding. For example, this approach allows for a systematic evaluation of the importance of the positions of the various atomic states on the metal atom for the bonding. Also, the effects of a continuous increase of the ionization potential and an increase of the number of *d*-electrons of the metal can be investigated by going from left to right across the row in the periodic table.

The second row transition metal hydrides have already been studied by Langhoff et al. [3] and more recently by Balasubramanian [8], and the present study will not add many new aspects to those studies. However, for completeness, the hydrides have been redone here using the present basis sets and methods, which are slightly different from the ones used in [3] and [8]. The geometries optimized in [3] have been used. Of the second row transition metal halides only those of yttrium have been studied theoretically before [9], and comparison to that work will be given in the discussion below. Experimentally, two thermochemically determined bond strengths are quoted by Huber and Herzberg [10], one for yttrium fluoride and the other one for molybdenum fluoride.

2. Computational details

In the calculations reported in the present paper for the hydrides and halides of the second row transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme. All valence electrons, except the fluorine 2*s*- and chlorine 3*s*-electrons, were correlated using size consistent methods.

For the metals the Huzinaga primitive basis [11] was extended by adding one diffuse *d*-function, two *p*-functions in the 5*p*-region and three *f*-functions, yielding a (17*s*, 13*p*, 9*d*, 3*f*) primitive basis. The core orbitals were totally contracted [12] except for the 4*s*- and 4*p*-orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects [13]. The 5*s*- and 5*p*-orbitals were described by a double zeta contraction and the 4*d* by a triple zeta contraction. The *f*-functions were contracted to one function giving a [7*s*, 6*p*, 4*d*, 1*f*] contracted basis. For fluorine the primitive (9*s*, 5*p*) basis of Huzinaga [14] was used, contracted according to the generalized contraction scheme to [3*s*, 2*p*]. One even-tempered *p*-function with exponent 0.0795 and one *d*-function with exponent 1.0 was added. For chlorine a similarly contracted basis was used based on the primitive (12*s*, 9*p*) basis of Huzinaga [14], and including an even-tempered diffuse *p*-function with exponent 0.044. Two *d*-functions with exponents 0.95 and 0.32 were added [15]. For hydrogen the primitive (5*s*) basis from [16] was used, augmented with one *p*-function with exponent 0.8 and contracted to [3*s*, 1*p*]. These basis sets are used in the energy calculations for all systems.

For the present small diatomic systems it is trivial to extend the basis set further. However, for the present purpose where the goal is to study ligand effects in larger transition metal complexes, it is more interesting to investigate even smaller basis sets than the ones described above. Larger calculations, which can be used for calibration purposes, have anyway already been done by Langhoff et al. for the yttrium halides [9]. Instead, comparative calculations have been done where the *d*-functions on the halides have been removed to find out if this is a sufficient description of the metal halide bonding.

In the geometry optimizations, performed at the SCF level, somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt [17] was used. The frozen 4*s*- and 4*p*-orbitals are described by a single zeta contraction and the valence 5*s*- and 5*p*-orbitals are described by a double zeta basis and the 4*d*-orbital by a triple zeta basis, including one diffuse function. The rest of the atoms are described by standard double zeta basis sets, with the chlorine core replaced by an ECP [18].

The correlated calculations were in most cases performed using the Modified Coupled Pair Functional (MCPF) method [19], which is a size-consistent, single reference state method. The zeroth order wave-function was in these cases determined at the SCF level. In a few cases a CASSCF (Complete Active Space SCF) treatment [20] is necessary to properly describe correct diatomic symmetry. In those cases multireference ACPF (Average Coupled Pair Functional) [21] calculations were performed for the dynamical correlation treatment. The metal valence electrons (4*d* and 5*s*) and the five *p*-electrons on the halides were correlated. Since the valence 2*s*-orbitals on fluorine and 3*s*-orbitals on chlorine rotated with the metal 4*p*-orbitals to the left in the row, these electrons were not correlated. Since these orbitals rotate with each other it appears that it is more consistent to consider all these electrons, or none of them, as core electrons. In addition, the calculations for the yttrium halides in [9] show that a proper account of correlation of the halide *s*-electrons does not notably improve the description of the bonding in these systems. Relativistic effects were accounted for using first order perturbation theory including the mass-velocity and Darwin terms [2].

An almost general, and rather surprising, finding can finally be mentioned for the treatment of second row transition metal complexes. It has been found that the single reference state correlation treatment is remarkably accurate for these systems [3–7]. In the present study this finding is extended to systems where a single reference treatment may be considered not to work in principle. For example, the $^4\Phi$-state of RuF should at the CASSCF level be described by two determininants $[\sigma^1\pi^1_{b1}\delta^1_{a2}]$ and $[\sigma^1\pi^1_{b2}\delta^1_{a1}]$ (in C_{2v}) with equal weights using cartesian Gaussian functions. If proper symmetry is not enforced on the orbitals, the one configuration SCF calculation will almost perfectly compensate for the near degeneracy problem by forming orbitals in the first symmetry which are linear combinations of σ and δ orbitals. Therefore, the single reference MCPF treatment gives a binding energy which differs by only 0.5 kcal/mol out of a total of 87.2 kcal/mol compared to the proper two-configuration ACPF treatment. For larger systems, which do not have perfect near degeneracy by symmetry, this type of compensation effect at the single reference level can not even be considered to be incorrect in principle and will probably occur frequently.

3. Results and discussion

The main result of the present study is shown in Fig. 1 as the trend of the binding energies of the hydrides and the halides for the second row transition

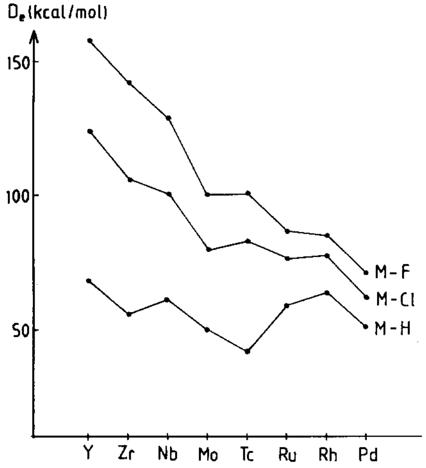

Fig. 1. Calculated bond strengths between second row transition metal atoms and hydrogen, fluorine, and chlorine

metal atoms. The detailed results for the hydrides are given in Table 1, for the fluorides in Table 2 and for the chlorides in Table 3.

The main trends of the binding energies are clearly demonstrated in Fig. 1. The binding energies for the halides decrease significantly going from left to right in the periodic table, whereas those of the hydrides are much more constant. The largest variation is displayed by the fluorides where the binding energy for PdF

Table 1. Bond distances (Å), populations and binding energies (kcal/mol) for the second row transition metal hydride systems

Metal (M)	State	M-H[a]	M(q)	4d	5s	5p	D_e
Y	$^1\Sigma^+$	1.96	+0.13	0.80	1.62	0.43	68.0
Zr	$^2\Delta$	1.86	+0.13	1.98	1.54	0.34	56.0
Nb	$^5\Delta$	1.79	+0.14	3.75	0.93	0.15	61.1
Mo	$^6\Sigma^+$	1.75	+0.13	4.92	0.82	0.09	50.4
Tc	$^5\Sigma^+$	1.67	+0.11	5.46	1.24	0.14	42.3
Ru	$^4\Sigma^-$	1.65	+0.05	7.09	0.73	0.08	58.9
Rh	$^3\Delta$	1.57	+0.06	8.18	0.62	0.09	64.1
Pd	$^2\Sigma^+$	1.54	+0.07	9.33	0.46	0.08	51.1

[a] Taken from Langhoff et al. [3]

Table 2. Bond distances (Å), populations and binding energies (kcal/mol) for the second row transition metal fluoride systems

Metal (M)	State	M-F	M(q)	4d	5s	5p	D_e
Y	$^1\Sigma^+$	2.00	+0.49	0.55	1.60	0.30	158.1
Zr	$^2\Delta$	1.93	+0.44	1.70	1.50	0.30	141.9
Nb	$^5\Pi$	1.97	+0.53	3.48	0.79	0.15	129.1
Mo	$^6\Sigma^+$	2.00	+0.58	4.70	0.55	0.12	100.4
Tc	$^7\Sigma^+$	2.05	+0.59	5.14	0.91	0.32	101.2
Ru	$^4\Phi$	^{2}.05	+0.60	7.04	0.18	0.13	87.2
Rh	$^3\Delta$	2.04	+0.63	8.01	0.17	0.13	85.0
Pd	$^2\Sigma^+$	2.01	+0.60	9.09	0.12	0.10	71.2

Table 3. Bond distances (Å), populations and binding energies (kcal/mol) for the second row transition metal chloride systems

Metal (M)	State	M-Cl	M(q)	4d	5s	5p	D_e
Y	$^1\Sigma^+$	2.52	+0.40	0.63	1.57	0.35	124.3
Zr	$^2\Delta$	2.42	+0.36	1.88	1.39	0.32	106.1
Nb	$^5\Pi$	2.46	+0.49	3.70	0.63	0.15	101.0
Mo	$^6\Sigma^+$	2.49	+0.55	4.92	0.36	0.14	79.7
Tc	$^7\Sigma^+$	2.54	+0.54	5.13	0.94	0.36	82.8
Ru	$^4\Phi$	2.49	+0.55	7.05	0.20	0.15	76.5
Rh	$^3\Delta$	2.46	+0.56	8.03	0.20	0.16	77.8
Pd	$^2\Sigma^+$	2.42	+0.54	9.10	0.16	0.14	62.4

is only 45% of the one for YF and with an absolute decrease between YF and PdF of 86.9 kcal/mol. For the chlorides the corresponding decrease is 61.9 kcal/mol and the binding energy of PdCl is 50% of the one for YCl. It is clear that at least part of these trends can be explained by a large contribution of ionic bonding for the halides as demonstrated by the Mulliken populations in the tables. However, the difference in the binding energies between YH and YF (90.1 kcal/mol) is far larger than can be explained on the basis of the difference in electron affinities of H and F or differences in the bond distances of YH and YF. The electron affinity of hydrogen is 0.75 eV and the one of fluorine is 3.45 eV. The bond distance difference between YH and YF is very small of 0.04 Å and YH has the shorter distance. If the binding would be totally ionic these differences would imply a binding energy difference between YF and YH of 59 kcal/mol which is much smaller than the actual difference. It is thus clear that other covalent and repulsive effects are also of importance for the binding energy difference. Another argument for other important effects is given by the binding energy difference between the halides for the metal atoms to the left and for those to the right. The difference in ionization potential between palladium and yttrium is 2.02 eV (46.6 kcal/mol), while the binding energy difference between YF and PdF, which have very similar bond lengths, is 86.9 kcal/mol.

In recent studies where reactions between water, ammonia and methane and second row transition metal atoms are compared [23, 24, 4], it has been shown that the lone pairs play a significant role for the energetics of the reactions. The interaction between ligand lone pairs and transition metal atoms have both repulsive and attractive components. The repulsion between the lone pairs and the metal 4d-electrons increases from left to right as the number of 4d-electrons increases. The attractive component appears between the lone pairs and empty 4d-orbitals to the left by donation of electrons from the ligand to the metal. In the previous studies it was found that already a single occupation of a 4d-orbital essentially removes the donation and thus also this attraction. Therefore, a large sudden decrease in exothermicity in the ammonia reaction was found in going from niobium to molybdenum. It can be concluded that the same type of both attractive and repulsive interactions between the halide lone-pairs and the metal 4d-orbitals are responsible for a large part, probably about half, of the binding energy differences displayed in Fig. 1.

One indication of the rather complex nature of the interaction between the halides and the transition metal atoms can be seen on the metal charges in the different tables. For the hydrides the positive charge on the metal decreases going from left to right in the periodic table, which is expected based on the increasing ionization potential to the right. The metal charge is rather small indicating a dominatingly covalent interaction for the hydrides. The charge increases significantly for the halides in line with the more ionic bonding for these systems. However, in particular for the fluorides, the positive charge on the metal *increases* going to the right even though the ionization potential *increases* for these atoms. The reason for this is clearly that back-donation of charge from the ligand to the empty metal $4d$-orbitals to the left more than compensates for the fact that these metal atoms have lower ionization potentials. A similar indication of strong attractive lone pair interactions can be seen on the variation of the bond distances. For the hydrides the bond distances decrease by 0.4 Å from YH to PdH in line with the smaller radii of the atoms to the right. In contrast, for the halides the bond distances are almost constant going across the row. Again, the attractive lone pair interaction with the empty $4d$-orbitals to the left compensates for the fact that the radii of these atoms are larger. Very similar effects have also been seen for the metal-oxygen and metal-nitrogen bond distances for the insertion products of the reactions with water and ammonia, respectively [23, 24].

There are also variations in the binding energies across the periodic table which are due to differences in promotion energies and loss of exchange energies. The size of these effects depend on the ground states of both the atoms and the diatomic molecules. As can be seen in Fig. 1 these effects are much less pronounced for the halides than for the hydrides simply because they are hidden behind the large general decrease in binding energies for the halides going from the left to the right in the row. For the hydrides the ground states are determined by an optimal mixing of atomic s^1- and s^2-states [3, 8]. Since a very careful work has already been done for the hydrides in these previous studies no particular effort was invested in order to study different states for these systems. However, a few of the more controversial cases were studied and the assignment of the ground states made by Balasubramanian [8] was confirmed, at least at the present level of accuracy. Thus, the $^4\Sigma^-$ state of RuH was found to be the ground state in favour of the $^4\Phi$ state. Also, the $^5\Pi$ state of NbH was found to be very close to the $^5\Delta$ state, but the latter state was found to be slightly lower in energy. However, as pointed out in [8], these two states are so close in energy that spin-orbit effects should ideally be taken into account for a proper assignment of ground state. This was done in [8] but has not been done here.

Most of the ground states for the halides are the same as for the hydrides but there are some exceptions. The most dramatic, and also illustrative difference, occurs for technetium. The hydride has a $^5\Sigma^+$ ground state but the halides have a $^7\Sigma^+$ ground state. The excitation energy for TcF to the lowest quintet state, which is a $^5\Delta$ state, is as high as 26 kcal/mol. This difference between the hydrides and the halides is easy to understand. The bond in the hydride is mainly covalent with metal $5s$-character. The lowest state that can form an s-bond is the ^6D ($4d^65s^1$) state, which will thus form a quintet hydride state. The atomic excitation energy to reach this state is 0.4 eV and there are therefore also large contributions from the ^6S ($4d^55s^2$) ground state of the atom. In contrast, the bonding in the halides are predominantly ionic. The ground state of the technetium ion is the ^7S ($4d^55s^1$) state. Since F^- and Cl^- will form closed shells, this leads to septet ground states for the technetium halides. Another illustrative difference between the hydrides and the halides occurs for niobium. As already mentioned, the $^5\Delta$ and the $^5\Pi$ states are almost degenerate for NbH, with the former state slightly lower in energy. For the halides the repulsion between the metal 4*d*-electrons and the lone-pairs of the halides becomes a dominating effect and it is therefore clear that it is more advantageous to keep a metal $4d_\pi$ orbital empty rather that a $4d_\delta$ orbital. The interaction between the empty $4d_\pi$ orbital and the fluorine lone pair in that symmetry will then be attractive through electron donation rather than repulsive. Since the interaction between the halides and the metal atoms should be strongest in the Σ symmetry, a $^5\Sigma^+$ state with an empty σ orbital might even have been expected. However, this leads to a loss of covalent bonding which requires *sd*-hybridization. A secondary effect of this *sd*-hybridization is that the repulsion in the Σ symmetry is efficiently avoided. Finally, there is also a difference in ground state for the hydrides and the halides for ruthenium, which is more intricate to understand. For RuH the ground state is $^4\Sigma^-$ whereas the halides have a $^4\Phi$ ground state. For the atoms both these states have an average of one singly occupied 4*d*-orbital in each of the Σ- Π- and Δ-symmetries, so there is not any possibility to differentiate repulsive effects for the two states on this simple ground. The choice of ground states must instead be based on unequal preference of the two states to mix with covalent and ionic configurations, where mixing in of ionic configurations is more important for the halides than for the hydrides. Another point concerning the ground state of RuF should finally be noted. As mentioned above, the ground state of RuF is assigned as $^4\Phi$, but at the present level of accuracy the $^6\Sigma^+$ state is actually slightly lower. However, there is a very large correlation effect favouring the $^4\Phi$ state and in a higher level treatment this state will therefore most certainly be lower and is therefore assigned as the ground state in the tables and in the figure. This problem does not appear for RuCl which has the $^4\Phi$ state as ground state already at the present level of accuracy.

The present results for the binding energies of yttrium and molybdenum fluoride can be compared to two thermochemically determined values [10]. The experimental result for YF of 110.7 kcal/mol is much lower than both the present value of 158.1 kcal/mol and the one determined by Langhoff et al. [9]. It can safely be concluded that the experimental result is too low. The thermochemical value for MoF of 110.2 kcal/mol is on the other hand slightly higher than the present result of 100.2 kcal/mol. Considering probable errors due to basis set deficiencies and configuration space limitations it is likely that the correct result should be somewhere in between the calculated and experimental value, probably in the region around 105 kcal/mol.

Since the present results should constitute a starting point for studies of ligand effects on reactivity of larger transition metal complexes it is of interest to investigate the possibility of using even smaller basis sets for the halides. All the present metal halides were therefore redone without *d*-functions on the halogens. This could appear as a possibly reasonable approximation for fluorine, but might be expected to be too drastic for the second row atom chlorine. In addition, the electron accepting ability of the 3*d*-orbitals of chlorine is often emphasized as an important property of chloride ligands. However, even through there is a marked effect of taking away the halogen 3*d*-funtions on the total binding energies of the metal halides, this effect is quite constant across the row and it is not much larger for the chlorides than for the fluorides. For the fluorides the effect is a lowering of the binding energies by 11.7 ± 1.1 kcal/mol including all the metals and for the chlorides the effect is

14.2 ± 1.1 kcal/mol. A large part of this decrease can as expected be traced to an inferior description of the electron affinity of the halogen atoms. For fluorine the electron affinity decreases by 7.2 kcal/mol when the *d*-functions are taken away. The remaining 5 kcal/mol should be due to deficiencies in the description of covalent and electron donation effects. It can further be concluded that the small difference between the effects on the fluorides and the chlorides does not support any major differences in the bonding of these ligands which should be due to actual 3*d*-orbital participation in the bonding for the chlorides.

For future discussions of ligand effects in larger complexes, it is of some interest to study the back-donation effects more in detail. In particular, it might be expected that chloride as a ligand should be a stronger π-donor than fluoride. However, any such tendency is not supported by the population analysis. Instead, the π-donations into empty 4*d*-orbitals of the metal are remarkably similar for the chloride and fluoride ligands. For example, for YF the π_x donating orbital has a F(2*p*) contribution of 1.83 electrons, an Y(5*p*) contribution of 0.02, an Y(4*d*) contribution of 0.09 electrons, and an Y(5*f*) contribution of 0.03 electrons at the MCPF level. The corresponding populations of YCl are for Cl(3*p*) 1.82 electrons, for Y(5*p*) 0.03 electrons, for Y(4*d*) 0.08 electrons and for Y(5*f*) 0.02 electrons. The π populations for the fluorides and chlorides of the other metals show a similar high degree of similarity. Also, since the total charges in the fluorides and the chlorides are quite similar, the σ donations must also be similar. It appears as if a possibly higher tendency for the chloride of donating its electrons is exactly cancelled by the longer bond distances for the chlorides. This cancellation effect is probably not a coincidence but is instead a result of the balance of effects which determines the final bonding in the systems.

Already based on the constant and rather small contribution from halogen *d*-functions to the bond strengths, it can be concluded that the present basis sets should be adequate for the present purpose. To further confirm this conclusion the present results can be compared to the calculations by Langhoff et al. [9] for yttrium fluoride and chloride. They use a larger basis set than the one used here, including *f*-functions on the halogens and three uncontracted *f*-functions on the metal. Another difference to the present work is that an effective core potential was used for the metal. With this basis they obtain a binding energy (D_e) for YF of 155.9 kcal/mol and for YCl of 124.1 kcal/mol. The present results are 158.1 kcal/mol and 124.3 kcal/mol, respectively.

4. Conclusions

The present work has been done mainly as a first step in a comparative study of hydrides and halides as ligands in reactions involving transition metal complexes. At this preliminary stage it is difficult to draw any major conclusions on this point but there are already a few implications from the present results. For example, for the metal insertion products of methane or hydrogen, it can be expected that halide ligands could be stabilizing compared to hydrides when ionic effects are dominating the bonding and destabilizing when covalent effects are dominating. When covalent effects dominate the bonding, as for the atoms to the right of the row, it is expected that there will be a competition for bonding electrons between the halide ligands and the hydride or methyl ligands, which should have a destabilizing effect. This should also be the case when there are many halide ligands. When ionic effects become more important, as they do for the atoms to the left in the row, the halides could help in stabilizing a strongly positive metal atom and thus also stabilize the ionic part of the bonding to hydride and methyl groups. Another tentative conclusion which can be drawn is that donation backdonation effects involving the ligand 3*d*-orbitals are not likely to be of major importance for chloride ligands. This conclusion is based on the small difference of the effect of *d*-functions on fluorine and chlorine and the constancy of this effect across the row. The constancy implies that the effect should be localized on the halide and therefore not have any important chemical consequences when the metal interacts with other systems. Another indication that the 3*d*-orbitals of the chloride ligands do not give any additional preference for donation and back-donation is given by the present population analysis, where the amount of *p*-donation is remarkably similar between fluoride and chloride ligands.

The present study has shown that the metal halide bond strengths vary much more across the periodic table than the metal hydride bond strengths. There are two major origins of this increased variation for the halides. First, the bonding in the halides is much more ionic than for the hydrides which means that the variation of the ionization potential of the metal atoms enters more or less directly in the final bond strengths. Secondly, and of about equal importance, the direct interaction between the metal 4*d*-orbitals and the lone pairs of the halides have both repulsive and attractive components which vary strongly across the row. The attraction occurs only for the atoms to the left which have empty 4*d*-orbitals and which can thus receive electrons from the halide lone-pairs. The repulsion occurs between the metal 4*d*-electrons and the lone-pairs and increases with the number of 4*d*-electrons to the right. All these effects combine to give much larger binding energies for the halides to the left than to the right.

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