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Crystal Field Interpretation of Some Activity Patterns

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Crystal field stabilization energies have been calculated for various first series transition metal oxides. The geometric ligand configurations considered are the transition from a square pyramid to an octahedral configuration due to a chemisorbed O^{2-} ion. The metal oxides considered show a clearer pattern in their crystal field stabilization in certain other geometric structures where the chemisorbed O^{2-} ion does not change the symmetry of the complex. The crystal field effects obtained agree well with observed catalytic activity patterns.

INTRODUCTION

First series transition metal oxides are frequently used as catalysts for oxidation reactions. The application of the crystal field theory to first series transition metal oxides requires bonds of predominantly ionic character between the metal and the oxygen. This assumption seems to have considerable justification (*1*, *2*). The additional assumption of redox couples appears to be a useful model for oxidation reactions.

Considering oxidation reactions, Dowden and Wells (*1*) were first to show that a remarkable relation exists between the catalytic activity and the crystal field stabilization for various first series transition metal oxides. Their work is based on the idea that a chemisorbed O^{2-} ion changes the symmetry as well as the strength of the crystal field affecting the transition metal ion. However, important configuration changes like the one from a square pyramid to octahedral symmetry seem to cause only very small increases or even decreases in the total stabilization energy for the various metal ions. Their calculation of the stabilization energies are based on a quantitative pattern for crystal field splittings presented by Basolo and Pearson (*3*). There appears to be some confusion in respect to this crystal field splitting pattern for certain nonoctahedral symmetry cases. Hartmann and Fischer-Wasels (*4*), for example, reported a splitting for *D* terms of a Ni^{II} ion (not ground term) in square planar configuration which contradicts the quantitative pattern of Ref. (*3*), so do the results of Orgel (*5*) on the same term for tetrahedral configuration. Furthermore, Basolo and Pearson caution not to compare the splitting pattern of one symmetry case with another one quantitatively as done in Ref. (*1*). In this paper, the stabilization energy changes have been calculated for the transition from a square pyramid ligand configuration to an octahedral one. The results are compared to the results of Dowden and Wells for the same case.

Generally, an incoming O^{2-} ion causes a particular metal ion to split rather differently depending on the geometric configuration the metal ion was exposed to before. This implies a change of symmetry caused by the incoming O^{2-} ion. As a result, a different split term can be lowest for the metal ion before and after the O^{2-} ion has been chemisorbed. Therefore, it is difficult to make a fair comparison of the pertinent crystal field stabilization energies occurring for different metal ions without knowing the geometric configurations of the most effective active catalyst sites. In order to avoid this difficulty, in this paper, configurations have also been considered where an incoming ligand does not change the symmetry of the crystal field and where the part of the stabilization energy due to the incoming ligand adds linearly to the total stabilization energy of the transition metal ion. This seems to provide a clearer comparison of the stabilization energies for different metals. The results strongly support the original claims of Dowden and Wells.

This work is confined to oxidation reactions catalized by the oxides of the following first series transition metals: $\mathrm{Ti^{III}}$, $\mathrm{Ti^{II}}$, $\mathrm{V^{IV}}$, $\mathrm{V^{III}}$, $\mathrm{V^{II}}$, $\mathrm{Cr^{III}}$, $\mathrm{Cr^{II}}$, $\mathrm{Mn^{IV}}$, $\mathrm{Mn^{III}}$, $\mathrm{Mn^{II}}$, $\mathrm{Fe^{III}}$, $\mathrm{Fe^{II}}$, $\mathrm{Co^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{III}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$.

CRYSTAL FIELD CALCULATIONS

Besides octahedral and square pyramidal ligand configurations being of O_h or C_{4v} symmetry, additional configurations are considered here which show the following characteristic property. The O^{2-} ligand of the original catalyst positioned on the main symmetry axis is assumed to display an overwhelming influence on the metal ion compared to all other ligands so that the stabilization energy caused by the chemisorbed O^{2-} ion also positioned on the main axis will linearly add in full to the total stabilization energy of the metal ion. Such a configuration is realized by a single metal ion above a regular crystal plane or by a single metal ion at a corner of a cubic body centered lattice. C_{4v} symmetry has been assumed for simplicity. However, the change of stabilization energy due to an incoming O^{2-} ion on the main axis turns out to be the same, to a first approximation, for any pertinent symmetry case of the type considered.

The crystal field theory formalism used is very similar to the one of Ref. (*6*). The weak field method has been followed throughout this paper. The formalism is given by Condon and Shortley (*7–9*).

The metal ions investigated have S, D, F terms as ground terms. Since S terms (resulting from d^5 as in $\mathrm{Fe^{III}}$ or $\mathrm{Mn^{II}}$ or from d^{10} as in $\mathrm{Cu^{I}}$ or $\mathrm{Zn^{II}}$) do not split in any crystal field, these ions show no stabilization effects at all in weak field method calculations. D and F terms split under the influence of O_h and C_{4v} fields in the following way:

$$D \xrightarrow{O_h} T_{2g} + E_g, \qquad D \xrightarrow{C_{4v}} A_1 + B_1 + B_2 + E,$$

$$F \xrightarrow{O_h} T_{1g} + T_{2g} + A_{2g}, \qquad F \xrightarrow{C_{4v}} A_1 + B_1 + B_2 + 2E.$$

Ballhausen (7) presents the stabilization energy ΔE caused by octahedral ligand fields for all metal ions considered

$$d^1,\ d^6 \rightarrow \Delta E = -4Dq$$

$$d^2,\ d^4,\ d^7,\ d^9 \rightarrow \Delta E = -6Dq$$

$$d^3,\ d^8 \rightarrow \Delta E = -12Dq$$

where 10 Dq is defined as the amount of splitting of a single d-electron in an octahedral ligand field. A negative value of ΔE indicates stabilization.

To obtain the expressions for ΔE in the case of C_{4v} symmetry, the proper linear combinations of atomic eigenfunctions belonging to these irreducible representations are calculated following the method of Bethe (*10*). The atomic eigenfunctions obtained are subsequently replaced by antisymmetrized products of one-electron eigenfunctions. Condon and Shortley (*11*) present a formula for changing the pertinent integrals of products of one-electron eigenfunctions into sums of one-electron integrals of which only the following seven do not vanish:

$$\int 2^* V_s 2\, d\tau; \quad \int -2^* V_s -2\, d\tau;$$

$$\int 1^* V_s 1\, d\tau; \quad \int -1^* V_s -1\, d\tau;$$

$$\int 0^* V_s 0\, d\tau; \quad \int 2^* V_s -2\, d\tau;$$

$$\int -2^* V_s 2\, d\tau.$$

where $\int \ldots d\tau$ indicates integration over the whole space. V_s is the perturbation operator representing the ligand field. 2, 1, 0, −1, −2, are the complex d-electron eigenfunctions with the magnetic quantum number 2, 1, 0, −1, −2 (*12*). The asterisk refers to the conjugated complex nature of this one-electron eigenfunction.

One has also to consider the constant amount of shifting of all split terms resulting from the ground term of a free ion as explained by Ballhausen (*7*).

Slater type eigenfunctions are most commonly used in ligand field calculations due to their simplicity. Generally, the radial part of a Slater eigenfunction is considered as the least accurate part. These radial parts contain the Slater parameter *f* (*12*) and the distances *R* between central ion and ligand in higher powers. Unfortunately, the *f* and *R* values often cannot easily be obtained with sufficient accuracy. Therefore, to overcome these shortcomings of Slater's eigenfunctions, one commonly calculates any crystal field splitting or crystal field stabilization in terms of 10 *Dq* of the considered case. 10 *Dq* in terms of *f* and *R* is given by

$$10Dq = 525\frac{n}{f^4R^5}, \qquad (1)$$

for all ions with 3*d*-electrons, with *n* being the number of negative charges of the ligand considered.

$$f^2R^3 = (f^4R^5)^{3/5} \times \hat{f}^{-2/5}, \qquad (2)$$

where $\hat{f}$ are the proper *f* values calculated by Slater's rule (*12*). This way, the values of $1/f^2R^3$ and $1/f^4R^5$ used, i.e., the radial parts of the pertinent eigenfunctions, are obtained semiempirically and are more accurate than in an a priori calculation of the Slater eigenfunction. Table 1 contains the values used for f^2R^3, f^4R^5, and *Dq*, of which the latter are experimentally obtained from absorption spectra (*7, 13*). Whenever the *Dq* values for the oxides were unavailable, the *Dq* values for the corresponding octahedral hexa-aquo complexes were used as shown in Ref. (*1*).

All results for $\mathrm{Ti^{II}}$ have been omitted because of $\mathrm{Ti^{II}}$ complexes being unstable.

The one-electron integrals have a solution of the following general form for ion ligands:

$$P_0^{|0|}(\cos\vartheta)M_0\frac{n}{R} + P_2^{|0|}(\cos\vartheta)M_2\frac{n}{f^2R^3} + P_4^{|0|}(\cos\vartheta)M_4\frac{n}{f^4R^5},$$

where $P_n^{|0|}(\cos\ \vartheta)$ is the associated Legendre polynominal. ϑ is the angle formed by the main axis and the shortest connection between the pertinent O^{2-} ligand and the metal ion.

All terms with M_0 vanish for the calculation of the stabilization energies.

TABLE 1

VALUES OF f^2R^3, f^4R^5, AND *Dq* FOR DIFFERENT TRANSITION METAL IONS

Ion	f^2R^3 (a.u.)	f^4R^5 (a.u.)	*Dq* ($\mathrm{cm^{-1}}$)	Remarks
$\mathrm{Ti^{III}}$	241.6	11 350	2030	
$\mathrm{V^{IV}}$	190.5	8 864	2600	Extrapolated value
$\mathrm{V^{III}}$	237.8	12 226	1885	
$\mathrm{V^{II}}$	325.0	19 531	1180	
$\mathrm{Cr^{III}}$	232.0	12 804	1800	
$\mathrm{Cr^{II}}$	277.2	16 461	1400	
$\mathrm{Mn^{IV}}$		11 730		From crystal radius
$\mathrm{Mn^{III}}$	198.0	10 621	2170	
$\mathrm{Fe^{II}}$	309.0	23 047	1000	
$\mathrm{Co^{III}}$	193.3	11 640	1980	Reference 13
$\mathrm{Co^{II}}$	304.9	24 260	950	
$\mathrm{Ni^{III}}$	323.0	29 030		From crystal radius
$\mathrm{Ni^{II}}$	313.4	27 114	850	
$\mathrm{Cu^{II}}$	261.9	20 950	1100	

It is because of $P_n^{|o|}(\cos\vartheta)$ that the ligands on the main symmetry axis, i.e., $\vartheta = 0°$, cause strongest crystal field effects followed by the ligands with $\vartheta = 90°$. Any other ligands, with $\vartheta = 45°$ for example, show much smaller crystal field effects. It is due to this series of decreasing influence that those cases are realistic where one ligand on the main axis is of overwhelming importance.

Only considering the single chemisorbed O^{2-} ligand, the following M_2 and M_4 values are obtained for the seven aforementioned one-electron integrals

$$\left.\begin{array}{l} \int 2^*V_s2\,d\tau \\ \int -2^*V_s-2\,d\tau \end{array}\right\} M_2 = -4;\quad M_4 = 15,$$

$$\left.\begin{array}{l} \int 1^*V_s1\,d\tau \\ \int -1^*V_s-1\,d\tau \end{array}\right\} M_2 = 2;\quad M_4 = -60,$$

$$\int 0^*V_s0\,d\tau \Big\} \; M_2 = 4;\quad M_4 = 90,$$

$$\left.\begin{array}{l} \int 2^*V_s-2\,d\tau \\ \int -2^*V_s2\,d\tau \end{array}\right\} M_2 = 0;\quad M_4 = 0,$$

The M_2 and M_4 values for the case of a square pyramid ligand configuration are as follows:

$$\left.\begin{array}{l} \int 2^*V_s2\,d\tau \\ \int -2^*V_s-2\,d\tau \end{array}\right\} M_2 = 4;\quad M_4 = 37.5,$$

$$\left.\begin{array}{l} \int 1^*V_s1\,d\tau \\ \int -1^*V_s-1\,d\tau \end{array}\right\} M_2 = -2;\quad M_4 = -150,$$

$$\int 0^*V_s0\,d\tau \Big\} \; M_2 = -4;\quad M_4 = 225,$$

$$\left.\begin{array}{l} \int 2^*V_s-2\,d\tau \\ \int -2^*V_s2\,d\tau \end{array}\right\} M_2 = 0;\quad M_4 = 65.625,$$

Since the following equalities

$$\int 2^*V_s2\,d\tau = \int -2^*V_s-2\,d\tau;\quad \int 1^*V_s1\,d\tau = \int -1^*V_s-1\,d\tau;\quad \int 2^*V_s-2\,d\tau = \int -2^*V_s2\,d\tau,$$

are valid for the considered case, the final results for the stabilization energy due to a C_{4v} ligand field can be stated as follows:

$$d^1 \rightarrow {}^2D \tag{3}$$

$$\Delta E(^2A_1) = -\frac{2}{5}\int 2^*V_s2\,d\tau - \frac{2}{5}\int 1^*V_s1\,d\tau + \frac{4}{5}\int 0^*V_s0\,d\tau,$$

$$\Delta E(^2B_1) = +\frac{3}{5}\int 2^*V_s2\,d\tau - \frac{2}{5}\int 1^*V_s1\,d\tau - \frac{1}{5}\int 0^*V_s0\,d\tau + \int 2^*V_s-2\,d\tau,$$

$$\Delta E(^2B_2) = +\frac{3}{5}\int 2^*V_s2\,d\tau - \frac{2}{5}\int 1^*V_s1\,d\tau - \frac{1}{5}\int 0^*V_s0\,d\tau - \int 2^*V_s-2\,d\tau,$$

$$\Delta E(^2E) = -\frac{2}{5}\int 2^*V_s2\,d\tau + \frac{3}{5}\int 1^*V_s1\,d\tau - \frac{1}{5}\int 0^*V_s0\,d\tau.$$

$$d^2 \rightarrow {}^3F$$

$$\Delta E(^3A_1) = -\frac{2}{5}\int 2^*V_s2\,d\tau + \frac{4}{5}\int 1^*V_s1\,d\tau - \frac{2}{5}\int 0^*V_s0\,d\tau,$$

$$\Delta E(^3B_1) = +\frac{1}{5}\int 2^*V_s2\,d\tau - \frac{4}{5}\int 1^*V_s1\,d\tau + \frac{3}{5}\int 0^*V_s0\,d\tau - \int 2^*V_s-2\,d\tau,$$

$$\Delta E(^3B_2) = +\frac{1}{5}\int 2^*V_s2\,d\tau - \frac{4}{5}\int 1^*V_s1\,d\tau + \frac{3}{5}\int 0^*V_s0\,d\tau + \int 2^*V_s-2\,d\tau,$$

$$\Delta E(^3E') = +\frac{1}{5}\int 2^*V_s2\,d\tau + \frac{1}{5}\int 1^*V_s1\,d\tau - \frac{2}{5}\int 0^*V_s0\,d\tau,$$

$$\Delta E(^3E'') = -\frac{1}{5}\int 2^*V_s2\,d\tau + \frac{1}{5}\int 1^*V_s1\,d\tau.$$

$$d^3 \rightarrow {}^4F$$

all ΔE's are negative equal to the ΔE's of d^2.

$$d^4 \rightarrow {}^5D$$

all ΔE's are negative equal to the ΔE's of d^1.

$$d^5 \rightarrow {}^6S$$

$\Delta E({}^6A_1) = 0$

$$d^6 \rightarrow {}^5D$$

all ΔE's are equal to the ΔE's of d^1.

$$d^7 \rightarrow {}^4F$$

all ΔE's are equal to the ΔE's of d^2.

$$d^8 \rightarrow {}^3F$$

all ΔE's are negative equal to the ΔE's of d^2.

$$d^9 \rightarrow {}^2D$$

all ΔE's are negative equal to the ΔE's of d^1.

Ballhausen (*14*) presents a scheme for the splitting of a *d*-electron in tegragonal symmetry where the a_1 and b_2 split terms reverse energetic positions depending on the strength of the ligand field. This also contradicts a general quantitative splitting pattern as stated in Ref. (*3*). This situation sharply differs from a single 3*d*-electron in a field of O_h symmetry where the t_{2g} split term is always $4Dq$ below the original level and the e_g split term is always $6Dq$ above the original level.

The final results are presented in Table 2. ΔE is the crystal field stabilization energy in an octahedral or square pyramidal ligand field. $\Delta\epsilon$ is the difference between both, i.e., $\Delta\epsilon = \Delta E_{O_h} - \Delta EC_{4v}$. ΔE_1 is the increase of the crystal field stabilization energy due to a single incoming O^{2-} ion positioned on the main symmetry axis. The $\Delta\epsilon$ values of Dowden and Wells are presented for comparison. Negative ΔE, ΔE_1, $\Delta\epsilon$ values indicate stabilization.

DISCUSSION OF THE RESULTS

The results in Table 2 show that the stabilization energies for the transition from a square pyramid to an octahedral ligand configuration obtained in this paper differ considerably from the $\Delta\epsilon$'s reported

TABLE 2

VALUES OF ΔE, ΔE_1, $\Delta\epsilon$ OF DIFFERENT TRANSITION METAL IONS FOR O^{2-} LIGANDS (kcal/mole). The values in brackets are obtained with the strong field method.

Metal ion	No. of *d*-electrons	$\Delta E(O_h)$	ΔE (square pyramid)	$\Delta\epsilon$	$\Delta\epsilon$ (Dowden and Wells)	ΔE_1
Ti^{III}	1	−23	−27	+4	+2.9	−19
V^{IV}	1	−30	−34	+4		−24
V^{III}	2	−32	−32	0	+5.5	−15
V^{II}	3	−41	−21	−20	−7.0	−7
Cr^{III}	3	−62	−32	−30	−9.2	−10
Cr^{II}	4	−24	−26	+2	+12.0	−25
Mn^{IV}	3	−67	−35	−32		−11
Mn^{III}	4	−37	−38	+1	+17	−36
Mn^{II}	5	0	0	0	0	0
Fe^{III}	5	0	0	0	0	0
Fe^{II}	6	−12	−16	+4	+1.7	−15
Co^{III}	6	−23 [−54]	−29 [−31]	+6 [−23]	+3 [−21]	−24
Co^{II}	7	−16	−18	+2	+3.2	−11
Ni^{III}	7	−13	−16	+3		−10
Ni^{II}	8	−29	−15	−14	−4.6	−5
Cu^{II}	9	−19	−25	+6	+12	−25
Cu^{I}	10	0	0	0	0	0

by Dowden and Wells. Since no more refinements of the weak field method have been used here, the difference seems to be due to the general splitting pattern for a square pyramid configuration as discussed before. However, especially the $\Delta E(O_h)$ results are subject to various corrections. All d^4 and d^9 metal ions are strongly stabilized in O_h fields by the Jahn-Teller effect. This would drop the energy state for $\mathrm{Cr^{II}}$, $\mathrm{Mn^{III}}$, $\mathrm{Cu^{II}}$ sufficiently so that $\Delta\epsilon$ will be of negative value. Since for $\mathrm{Ni^{III}}$ and $\mathrm{Mn^{IV}}$ crystal radii have been used, the results are of lesser accuracy. Apparently, $\mathrm{V^{IV}}$ forms "octahedral" complexes, where one $\mathrm{O^{2-}}$ ion is considerably closer to the metal than the others. $\mathrm{V^{III}}$, on the other hand, shows a superposed trigonal component in its octahedral complexes. The unrealistically large positive value of $\Delta\epsilon$ for $\mathrm{Co^{III}}$ is due to the fact that most octahedral complexes have singlet split terms as ground terms. A strong ligand field causes an excited ^1G or ^1I term of the free ion to split so much that its lowest split term lies lower than the lowest split term of the ^5D term which is the ground state of a free $\mathrm{Co^{III}}$ ion. It is more convenient to calculate the splitting of ^1G and ^1I terms by using the strong field method. The differences between weak field and strong field results are here essentially due to the fact that two different split terms are considered. However, strong field calculations on the quintet case and the singlet case for a square pyramid lead to similar results as shown in Table 2. $\mathrm{Fe^{II}}$ displays the same behavior as $\mathrm{Co^{III}}$ to a somewhat lesser extent.

Besides the arguments as presented in the introduction, it becomes evident that many strong distortions like the Jahn-Teller effect affect complexes of different symmetry to a very different extent. Therefore, a case without symmetry change seems to be much more suited for comparing crystal field stabilization. The ΔE_1 values in Table 2 appear to be much more coherent than the $\Delta\epsilon$ values. If one assumes that the oxidation reactions considered involve a redox couple of the catalyst metal, a series with decreasing ΔE_1 can be stated:

$$\mathrm{Mn^{III}} > \mathrm{Cu^{II}} > \mathrm{Co^{III}} \approx \mathrm{V^{IV}} > \mathrm{V^{III}} > \mathrm{Ni^{II}} \approx \mathrm{Cr^{III}} \gg \mathrm{Fe^{III}} = 0$$

This series agrees well with the activity pattern reported by Klier (*2*) and Dowden and Wells (*1*). On the other hand, the corresponding series with decreasing $\Delta\epsilon$ substantially differs in the positions of $\mathrm{Cr^{III}}$, $\mathrm{V^{IV}}$, and $\mathrm{Mn^{III}}$.

The ΔE_1 values represent the crystal field energy change caused by one chemisorbed $\mathrm{O^{2-}}$ ion for most cases without symmetry change as mentioned before.

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