

Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. IX. Angular Overlap Model Calculations on Transition State Structures for Chromium(III) Substitution Reactions

O. MØNSTED

Chemistry Department I, Inorganic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

Linear correlations between enthalpies of activation for ligand hydrolysis reactions and single-ligand Δ -parameters, derived from visible absorption spectra, are found experimentally for the pentaamine- and the pentaquachromium(III) series of complexes. These empirical correlations have been rationalized using the angular overlap model of the ligand field, and in this way information on possible transition state structures for the substitution reactions has been obtained. It is concluded firstly that the metal-to-leaving-ligand bond is probably weakened but not completely broken in the transition state, and secondly that the most symmetrical transition state which accommodates the experimental data is one having square pyramidal coordination of the nonreacting ligands and symmetrical coordination of the entering and leaving ligand with respect to the fourfold axis defined by the five nonreacting ligands. Consequently the results reported here support the associative interchange mechanism proposed previously for these reactions.

The significance of the ligand field for the kinetic and thermodynamic behaviour of transition metal complexes is well established, and there are numerous examples of successful qualitative rationalizations of the variation in chemical behaviour of various metal ions with similar coordination spheres.¹

Most discussions of the influence of the ligand field on the kinetic behaviour of transition metal

complexes have been limited to exchange reactions which have been handled assuming ground state and transition state structures of high symmetry. Descriptions of structures of lower symmetry usually require many parameters unless simplifying assumptions are introduced. The angular overlap model² is one such attempt at simplification, and in combination with the assumption of ligand-parameter transferability between different complexes with identical central metal atoms the number of parameters necessary for a description of low symmetry structures may be greatly reduced. The recent availability of angular overlap model parameters for a variety of ligands coordinated to chromium(III)³ provides the possibility of carrying out a detailed treatment of the kinetic consequences of the ligand field from an experimental point of view. It should thus be possible to rationalize the empirical correlations which exist between spectroscopic and kinetic parameters, and thereby gain additional insight into the geometry of the transition states for substitution reactions.

METHOD OF CALCULATION

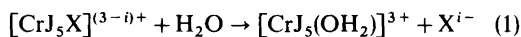
General equations facilitating the construction of ligand field matrices for all d^n configurations in all symmetries have recently been given.⁴ In this work the ligand field part of the energy matrices

for the quartet states* was generated using the relationship given in the footnote on p. 282 in Ref. 4, and the interelectronic part as described in Ref. 3. Tensorial parameters were calculated from angular overlap model parameters by use of the set of relations given by eqns. 61 and 62 in Ref. 4, with angular overlap matrix element products taken from Tables 3, 4, and 5 in Ref. 2.

RESULTS

A considerable number of empirical correlations between kinetic and spectroscopic parameters for chromium(III) complexes can be found in the literature. However, many of these are not well suited to a more detailed theoretical analysis since either positions of spectral bands are used as spectroscopic parameters, or rate constants are used as kinetic parameters, and neither band component sums nor the entropy part of the free energy can be handled by ligand field models at their present stage of evolution.

Consequently the chosen basis for the present investigation is the linear correlation between the enthalpies of activation for hydrolysis of ligands bound to a chromium(III) centre, as in the following generalized reaction scheme:



* Attempts have been made previously to account for the enthalpies of activation for chromium(III) substitution reactions in terms of ligand field effects only.⁵ This was only possible if a doublet excited electronic state was assumed for the transition state. However, comparisons with kinetic data for tripositive metal ions in which ligand field effects should be absent do not provide support for this approach. For the transition state geometries discussed in this paper electronic ground states are invariably quartet states.

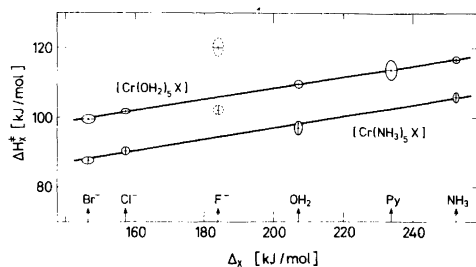


Fig. 1. Linear correlations between ΔH_X^\ddagger and Δ_X for pentaqua (\ominus -points) and pentaamminechromium(III) complexes (\oplus -points). Experimental values are indicated by contour ellipses of the probability density function drawn at the 68% probability level.

($J = \text{NH}_3$ or OH_2 ; $\text{X}^{i-} = \text{Br}^-$, Cl^- , (F^-), OH_2 , $\text{C}_5\text{H}_5\text{N}$ or NH_3 ; see Table 1), and the energy difference between the σ - and π -interactions between the substituted ligands and the central metal atoms

$$\Delta = \Delta'_\sigma - \Delta'_\pi$$

which for $J = \text{OH}_2$ has been noted previously.³ The correlations are shown in Fig. 1 and are described quantitatively in Table 2.

The existence of such correlations is strong evidence in favour of similar reaction mechanisms for these reactions, except in the case of hydrolysis of coordinated fluoride ion. This difference between the reactions of the coordinated fluoride ion and those of the other ligands has also been observed in other contexts and has been ascribed to protonation of the basic fluoride ligand in the transition state,⁶ a mechanism which is also known to operate for the hydrolysis of other basic ligands.

For the remaining ligands in each of the two series of complexes the differences in enthalpies of

Table 1. Enthalpies of activation for the ligand substitution processes of eqn. 1.

X^{i-}	$[\text{Cr}(\text{OH}_2)_5\text{X}]^{(3-i)+}$ kJ/mol	Ref. ^a	$[\text{Cr}(\text{NH}_3)_5\text{X}]^{(3-i)+}$ kJ/mol	Ref. ^a
Br^-	99.6 ± 1.3	6	88.8 ± 1.3	12,13
Cl^-	101.7 ± 0.8	7	90.4 ± 1.3	12,14
F^-	120.1 ± 2.5	7	102.1 ± 1.3	15
OH_2	109.6 ± 1.3	8	97.1 ± 2.0	16
Py^b	113.8 ± 2.9	9	—	—
NH_3	116.7 ± 0.8	10,11	105.9 ± 1.3	10,17

^a Where two references are given the enthalpy quoted is obtained as the weighted average of the two results.

^b In this table and throughout the paper Py is used as an abbreviation for pyridine.

Table 2. Estimated parameters (mean values \pm standard deviations upon the mean values) for the linear correlation between ΔH^\ddagger and Δ_X . (cf. Fig. 1).

Complexes	$\alpha^{a,b}$	$\beta^{a,b}$ kJ/mol
$[\text{Cr}(\text{NH}_3)_5\text{X}]^{(3-i)+}$	0.160 ± 0.007	65.1 ± 1.4
$[\text{Cr}(\text{OH}_2)_5\text{X}]^{(3-i)+}$	0.159 ± 0.005	76.6 ± 0.9

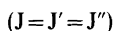
^a The functional relation between ΔH^\ddagger and Δ is given by $\Delta H^\ddagger = \alpha\Delta + \beta$, and α and β are estimated by minimization of $\sum(\Delta H^\ddagger - \alpha\Delta - \beta)^2 / [\sigma^2(\Delta H^\ddagger) + \alpha^2\sigma^2(\Delta)]$, where $\sigma^2(\Delta H^\ddagger)$ and $\sigma^2(\Delta)$ are the variances upon ΔH^\ddagger and Δ , respectively. ^b The two cases involving hydrolysis of coordinated fluoride have not been included in the calculations since these two reactions proceed *via* a different mechanism.⁶

activation are accurately described by differences in the ligand field parameter Δ of the leaving ligand. It therefore seems reasonable to assume that the major part of these enthalpy differences is the result of ligand field effects, and that other energetic consequences of the variation of the leaving ligand are of less importance.

This limits the following considerations to the α parameters of Table 2, which will be rationalized using the angular overlap model on a single reactant pair, a simplification of the treatment of an ensemble of reactants,¹⁸ which, however, since only the *variation* in a series of similar reactions is considered, should have little effect on the following conclusions.

The ligand field stabilization energy of the octahedral ground state of the $[\text{CrJ}_5\text{X}]^{(3-i)+}$ complex is $-(\Delta_J + \frac{1}{5}\Delta_X)$. If the leaving ligand, X, is completely dissociated in the transition state, the ligand field stabilization of this state will be independent of X irrespective of the transition state geometry. For the D mechanism it can thus be seen that the contribution to the enthalpy of activation from the ligand field of the X ligand is given by $\frac{1}{5}\Delta_X$. This differs from the experimentally observed variation (cf. Fig. 1 and Table 2), the implication being that the bond between the leaving ligand and the chromium(III) center is not completely broken in the transition state.

Evaluation of the role of the leaving ligand in transition states in which the bond between the metal centre and the leaving ligand is not completely broken is clearly a more difficult problem. The contribution from the ligand field to the enthalpy of activation for the ligand exchange process:



has previously been computed for all d^n electronic configurations, assuming a transition state of pentagonal bipyramidal geometry.¹ For the d^3 electronic configuration, however, the electronic ground state of such a transition state structure will be doubly degenerate, and such a geometry therefore cannot be expected to be stable for chromium(III) complexes.

All the evidence therefore points towards transition states with lower symmetry. The majority of substitution reactions of chromium(III) complexes which have been studied so far proceed with retention of configuration. Therefore, only *cis* attack of the entering ligand will be considered here, and two transition state structures based on such a restriction are shown in Fig. 2.

The two structures in Fig. 2 are easily handled by the angular overlap model: For the I_ϕ structure, the ligand field contribution, ΔL^\ddagger , to the enthalpy of activation is computed to be:

$$\text{I}_\phi: \Delta L^\ddagger = \frac{1}{20}(1 - 5 \cos 4\phi) \Delta_J \quad (3a)$$

Results for the II_ϕ structure are less easily reported since both the separation of Δ into contributions from σ - and π -bonding, as well as the inter-electronic repulsions are of importance. Results for selected sets of parameter values are shown graphically in Fig. 3 and may be compared with the values calculated from eqn. 3a for the I_ϕ structure. For ϕ values less than about 45° ΔL^\ddagger for the II_ϕ structure

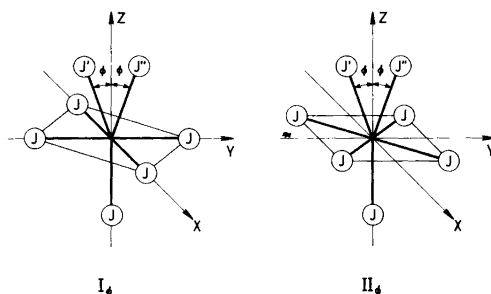


Fig. 2. Transition state structures discussed in the text. Both the leaving ligand, J', and the entering ligand, J'', lie in the YZ plane.

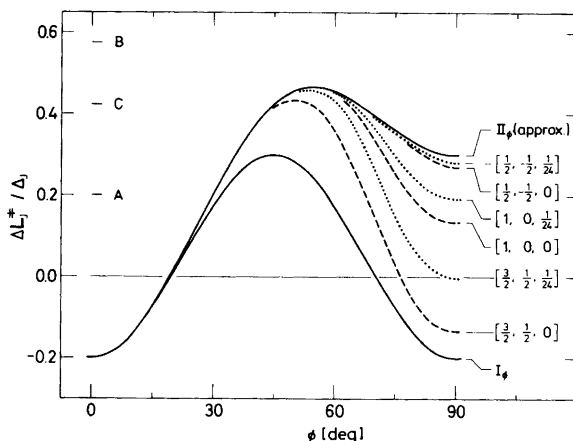


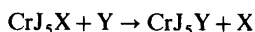
Fig. 3. Ligand field contribution to enthalpies of activation for exchange reactions of metal ions with a d^3 electronic configuration and octahedrally coordinated in the ground state with linearly ligating ligands. Parameters for the calculations without approximations for the Π_ϕ transition state are given in the form: $[\Delta'_o/\Delta_J, \Delta'_\pi/\Delta_J, b/\Delta_J]$. A, B and C are values for a tetragonal pyramid, a trigonal bipyramid and a pentagonal bipyramid, respectively.

is seen to be a function of ϕ and Δ only, and it may easily be verified that the approximation:

$$\Pi_\phi^*: \Delta L^\ddagger \sim \frac{1}{80} (19 - 20 \cos 2\phi - 15 \cos 4\phi) \Delta_J \quad (3b)$$

is valid for this range of values of ϕ .

The results given by eqns. 3a and 3b apply only to exchange processes of the type given by eqn. 2. However, most of the experimental material displayed in Fig. 1 is for reactions of the type:



For such reactions proceeding *via* transition states similar to those shown in Fig. 2, with $\text{X}=\text{J}'$ and

* Results for a transition state structure similar to Π_ϕ with $\phi = 45^\circ$ and $\phi = 54.74^\circ$ have been given previously.^{1,9} These results do not include the effects of interelectronic repulsion, and are limited to the value 2.0 for the crystal field parameter ratio, I^2/I^4 . In terms of angular overlap model parameters this ratio is:²

$$I^2/I^4 = (20 \Delta'_\sigma + 15 \Delta'_\pi) / 36 \Delta$$

which gives experimental values from 0.56 for ammonia coordinated to chromium(III) to 0.98 for fluoride coordinated to chromium(III).³ From Fig. 3 these values and the neglect of interelectronic repulsion are seen not to affect the 45° results but to limit the applicability of the results for the larger ϕ angle.

$\text{Y}=\text{J}''$, the following approximate expressions similar to those for the exchange process may be derived:

$$I_\phi: \Delta L^\ddagger \sim \frac{1}{40} [8 \Delta_X - (3 + 5 \cos 4\phi)(\Delta_X + \Delta_Y)] \quad (4a)$$

$$\Pi_\phi: \Delta L^\ddagger \sim \frac{1}{160} [32 \Delta_X + (3 - 20 \cos 2\phi - 15 \cos 4\phi)(\Delta_X + \Delta_Y)] \quad (4b)$$

It is immediately seen that the contribution to ΔL^\ddagger from the ligand which is substituted, X, is a function of Δ_X only, and it can readily be verified that values of ϕ of 26.5° and 25.4° , for the I_ϕ and Π_ϕ structures, respectively, reproduce the experimental variation of ΔH_X^\ddagger with Δ_X . The approximations inherent in both of the equations 4a and 4b have been tested by diagonalization of complete energy matrices for the quartet states of the d^3 electronic configuration. The results, which are depicted in Fig. 4, are seen to support the validity of the use of eqns. 4a and 4b.

The preceding results have all been obtained using the assumption of single ligand parameter transferability between different chromium(III) complexes. This assumption has been investigated previously in connection with parametrizations of the ligand field spectra of a variety of chromium(III) complexes, and for this purpose was found to be a useful approximation which permitted the estima-

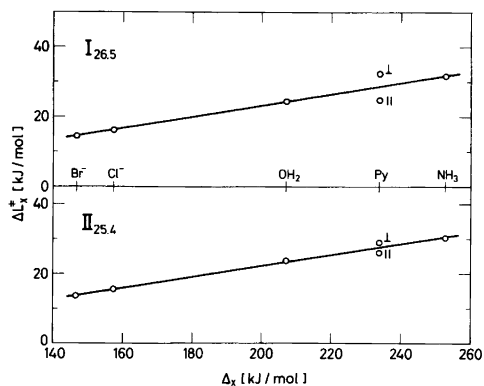


Fig. 4. Calculated values (○-points) for the ligand field contribution to enthalpies of activation for the ligand substitution processes given by eqn. 1, proceeding via the two transition states: I_ϕ with $\phi = 26.5^\circ$ and II_ϕ with $\phi = 25.4^\circ$. Single ligand Δ'_σ and Δ'_π parameters were taken from Table IV in Ref. 3. Differences between the two series of complexes, i.e. that with $J = \text{NH}_3$ and that with $J = \text{OH}_2$, are too small to be seen on the figure. The span of possible values for the pyridine complex, caused by the nonlinear ligation of the pyridine ligand,³ is between the two values indicated. For both transition state structures the upper value corresponds to the situation where the plane of the pyridine ring is perpendicular to the plane defined by the entering ligand, the metal atom, and the donor atom of the leaving ligand. The lower values are for the situation where these two planes are coplanar. A value for the angle between the two planes of about 45° will place the computed value for the pyridine complex on the indicated straight line, which has been drawn with the experimentally determined slope 0.160 (cf. Table 2).

tion of empirical Δ'_σ and Δ'_π parameters for a series of ligands.³ In the angular overlap model Δ'_σ and Δ'_π are empirical measures of σ - and π -interactions between a ligand and the central metal atom, and for a given ligand they are a function of the metal-to-ligand bond distance. Metal-to-ligand bond distances in octahedral ground states are rarely very dependent on the other ligands in the coordination sphere, and this may be one reason for the usefulness of the transferability assumption.

In the transition states for the substitution reactions studied here the metal-to-ligand bonds, although not completely broken, are almost certainly stretched compared to those in the ground state. The empirical ligand parameters cannot

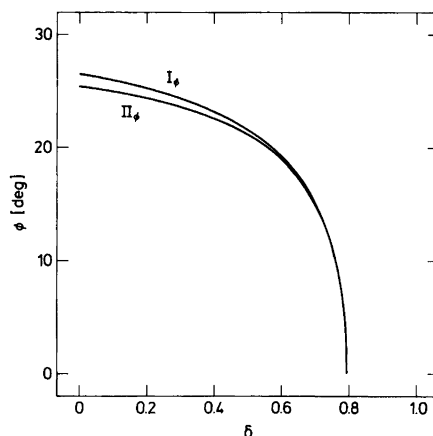


Fig. 5. Values of ϕ which rationalize the data of Fig. 1 and Table 2, drawn as a function of the degree of dissociation, δ , of the leaving ligand (cf. eqn. 5) in the I_ϕ and II_ϕ transition state structures.

therefore be expected to have the same values for the transition states as for the ground states. In this case ΔL^\ddagger may be expressed by a set of equations similar to 4a and 4b, but will contain the ligand Δ parameters for the transition states. These are not known but will be smaller than those for the ground states, and the degree of dissociation of the leaving ligand in the transition state, δ , may be defined as

$$\delta \equiv 1 - \frac{\Delta_{X(\text{TS})}}{\Delta_{X(\text{GS})}} \quad (5)$$

Defined in this way δ will have values between 0 ($\Delta_{X(\text{TS})} = \Delta_{X(\text{GS})}$) for the A mechanism to 1 ($\Delta_{X(\text{TS})} = 0$) for the D mechanism. Fig. 5 illustrates the relationship between values of δ and ϕ for the two different transition state structures which rationalize the experiments. Again the inaccessibility of a D mechanism is seen.

DISCUSSION

The analysis outlined in the preceding sections shows that it is possible to rationalize the variation in enthalpies of activation as a function of spectroscopic parameters of the leaving ligand on the basis of angular overlap model calculations on a single reactant pair. Complete dissociation of the leaving ligand does not occur in the transition state, and the

highest symmetry of the transition state is that attending symmetrical coordination of the entering and leaving ligand with respect to a fourfold axis defined by the five nonreacting ligands (*cf.* Fig. 2). A rather small angle between the bonds from chromium to the reacting ligands, $2\phi \lesssim 50^\circ$, is predicated by the quantitative calculations (*cf.* Fig. 5). It is thus plausible that the metal to ligand bonds, in order to compensate for an increase in ligand-ligand interactions, are stretched when the transition states are formed. That part of the net energetic consequences of such ligand motion which is a function of the leaving ligand is, however, apparently small when compared with the effects of the ligand field of this ligand, since Fig. 1 for the various ligands in question would otherwise be hard to understand. The total energy required to stretch the metal-to-ligand bonds to form the transition state is difficult to assess. It can be crudely estimated, however, that a number of the relevant energy contributions comprise a positive fraction of the ΔH^\ddagger values for the processes. Since ΔH^\ddagger and ΔH° are positively correlated this will have the effect of reducing acceptable δ values to numbers smaller than the 0.8 indicated by Fig. 5.

The material presented here is therefore additional evidence in favour of the associative interchange, I_a , mechanism for reactions of complexes within the pentaammine- and pentaquachromium(III) series. It is thus in agreement with conclusions reached from other types of evidence, in that the observation of negative volumes of activation for water exchange reactions and the existence of linear free energy relationships having slopes significantly smaller than 1.00 have been interpreted analogously.²⁰

The analysis carried out in this paper has been restricted to a transition metal ion with a d^3 electronic configuration but could easily be extended to other systems. At present, however, experimental values for angular overlap model parameters and substitution kinetic parameters for series of ligands bound to metal centers other than chromium(III) do not appear to be available. The practical application of such extended analyses is therefore limited at present, and it is not possible to say to what extent the behaviour of other metal ions will reflect the rather simple picture obtained here for chromium(III).

Acknowledgement. The author wishes to thank C. E. Schäffer for stimulating discussions on the ligand field part of this paper and Martin Hancock for revising the manuscript.

REFERENCES

1. Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd Ed., New York 1967.
2. Schäffer, C. E. *Struct. Bonding (Berlin)* 14 (1973) 69.
3. Glerup, J., Mønsted, O. and Schäffer, C. E. *Inorg. Chem.* 15 (1976) 1399.
4. Harnung, S. E. and Schäffer, C. E. *Struct. Bonding (Berlin)* 12 (1972) 257.
5. Spees, S. T., Perumareddi, J. R. and Adamson, A. W. *J. Am. Chem. Soc.* 90 (1968) 6626.
6. Guthrie, F. A. and King, E. L. *Inorg. Chem.* 3 (1964) 916.
7. Swaddle, T. W. and King, E. L. *Inorg. Chem.* 4 (1965) 532.
8. Stranks, D. R. and Swaddle, T. W. *J. Am. Chem. Soc.* 93 (1971) 2783.
9. Bakac, A. and Orhanovic, M. *Inorg. Chem.* 10 (1971) 2443.
10. Mønsted, L. and Mønsted, O. *Acta Chem. Scand.* A 28 (1974) 569.
11. Bakac, A., Butkovic, V. and Orhanovic, M. *Croat. Chem. Acta* 48 (1976) 35.
12. Data from: Levine, M. A., Jones, T. P., Harris, W. E. and Wallace, W. J. *J. Am. Chem. Soc.* 83 (1961) 2453, recalculated in Ref. 15.
13. Ramasami, T. and Sykes, A. G. *Inorg. Chem.* 15 (1976) 2885.
14. Duffy, N. V. and Early, J. E. *J. Am. Chem. Soc.* 89 (1967) 272.
15. Jones, T. P. and Phillips, J. K. *J. Chem. Soc. A* (1968) 674.
16. Swaddle, T. W. and Stranks, D. R. *J. Am. Chem. Soc.* 94 (1972) 8357.
17. Guastalla, G. and Swaddle, T. W. *Inorg. Chem.* 13 (1974) 61.
18. Glasstone, S., Laidler, K. J. and Eyring, H. *The Theory of Rate Processes*, 1st Ed., p. 153ff. New York 1941.
19. Hush, N. S. *Aust. J. Chem.* 15 (1962) 378.
20. Swaddle, T. W. *Coord. Chem. Rev.* 14 (1974) 217, and references therein.

Received November 7, 1977.